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SILICIDE COATINGS FOR TANTALUM AND COLUMBIUM ALLOYS

by
H.E. Shoemaker and A.R. Stetson

prepared for
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

AUGUST 1969

SOLAR
DIVISION OF INTERNATIONAL HARVESTER COMPANY
2200 PACIFIC HIGHWAY · SAN DIEGO, CALIFORNIA 92112

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Solar RDR 1557-2

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CONTRACT NAS3 – 9412

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FOREWORD

This Final Summary Report covers all work performed under NASA Contract NAS3-9412 from April 1, 1967 through December 31, 1968. The Solar internal number for this report is RDR-1557-2.

This contract was initiated between the NASA Lewis Research Center and Solar Division of International Harvester Company, for the development of protective coatings for tantalum - and columbium-base alloys and was an outgrowth of a program conducted under Contract NAS3-7276 (Ref. 1).

Technical direction was supplied by Mr. Robert E. Oldrieve, Project Manager, and Mr. Salvatore J. Grisaffe served as Research Advisor. Both are on the staff at NASA/Lewis Research Center. Mr. A. R. Stetson was the Program Director; Dr. R. T. Wimber served as Project Engineer from April 1 to October 31, 1967; and Mr. H. E. Shoemaker from November 1967 to program completion. Mr. F. J. Hodnick served as a support engineer throughout the program, and Mr. C. H. Saucer performed the electron microprobe analyses. Special recognition is given to Messrs G. T. Moyers and D. H. Creighton who performed the bulk of the application and testing of the program specimens. Metallography was performed by Mr. R. Hutting.

ABSTRACT

Twenty-six variations of silicided Mo-W-Ti-V modifier alloys were investigated for their ability to protect the T222 tantalum-base alloy. From this group, selected coatings were tested for their protection of the columbium-base alloy FS-85. The 20Mo50W15Ti15V modifier alloy yielded a silicide coating that provided protection (1) in cyclic furnace oxidation for more than 800 hours at 2400° F, (2) after ballistic impact at 170 ft/sec for 10 hours at 1600° F and 2400° F, (3) during 22 slow thermal cycles to 2300° F, and (4) in oxidation-erosion rig tests at Mach 0.85 and 2400° F for over 200 hours.

All of the coatings tested demonstrated the ability to provide significant oxidation protection to tantalum and columbium alloys when properly applied. It was proven advantageous to maintain the oxygen content as low as possible in the modifier coating. This was attained by adding the vanadium and titanium as hydrides to reduce their susceptibility to oxidation. Maintaining the combined percentages of titanium and vanadium near the 30 percent level in the slip was found to be desirable to produce a well bonded and sintered coating, but the sintering temperature had to be maintained sufficiently high (>2400° F) to remove a significant portion of these elements through vaporization. The retention of vanadium in the coatings was needed to prevent 1600° F oxidation failure.

The addition of small quantities of iron, nickel, or palladium to promote activated sintering greatly contributed to coating strength and improved coating/substrate bonding. The coatings were not satisfactory, however, when the sintering temperature and times were 2200° F and 1.5 hours, respectively. This caused retention of large amounts of titanium and vanadium or lessened coating/substrate interdiffusion. Prealloying the modifier instead of using a mixture of elemental powders offered no advantage.

The standard procedure for the duplex coating application throughout the program included slurry spraying of metallic elements and hydrides and vacuum sintering, which was followed with siliciding by pack cementation. To optimize the coating process, dip slurries were developed. The dip coatings provided less protection than those applied by spray techniques, but indicated the potential for development to provide equal or superior protection. Difficulties were encountered in obtaining protection of internal surfaces using the dip coating techniques.

CONTENTS

CONTENTS (Cont.)

ILLUSTRATIONS

ILLUSTRATIONS (Cont.)

ILLUSTRATIONS (Cont.)

ILLUSTRATIONS (Cont.)

ILLUSTRATIONS (Cont.)

TABLES

TABLES (Cont.)

1

INTRODUCTION

The objective of this program was the development of coatings for tantalum and columbium alloys which will withstand 3000 hours of advanced turbojet engine operation at temperatures appreciably higher than those permitted by the current superalloys. A further objective was to develop and evaluate coatings that will inhibit oxidation and interstitial contamination of T222 tantalum alloy and FS-85 columbium alloy upon cyclic exposure in the temperature range of 1800° F to 2400° F for a minimum of 300 hours. Under Contract NAS3-7276, between NASA and Solar, the 35Mo35W15Ti15V modifier alloy was applied to T222 specimens by slurry spray techniques (Ref. 1). Following vacuum sintering, high pressure pack siliciding yielded a coating which reproducibly and quite reliably provided more than 600 hours protection during cyclic oxidation testing at 1600° F and 2400° F. During the current program, the coating was modified by varying the proportions of the four elements in the modifier and by adding various other elements in minor quantities.

The program included extensive evaluation of the various coating compositions on the two substrate alloys. Tests included were furnace oxidation at 1600° F to 2400° F, bend tests, ballistic impact tests followed by oxidation, torch testing on selected coatings, mechanical property tests after 800 hours of oxidation testing, slow thermal cycling, and oxidation tests in the combustion products of JP-5 fuel and air at a velocity of Mach 0.85. Also included in the investigation were evaluation of process variables including activation sintering, oxygen content of modifier materials, particle size, and pre-alloying of the modifier alloy. Extensive investigation was performed on the influence of the silicon modifier ratio. Both dipping and spraying techniques were used in the application of the coating. The majority of the work utilized spray techniques, but a number of the configurations could only be coated by dipping.

2

SUMMARY

This program covers the extension of the coating development and evaluation activities initiated on Contract NAS3-7276 (Ref. 1) for the protection of T222 tantalum-base alloy and also extends the work to FS-85 columbium-base alloy. Coatings investigated were of the duplex type, i.e., an initial modifier alloy was applied by slurry techniques, vacuum sintered and subsequently pack silicided. Modifier alloys were primarily compositions containing W-Mo-Ti-V, but in some cases also contained additions of Fe, Pd, Ni or B to improve sintering or modify the oxide formed on the silicide. The sintered modifier thickness was controlled at approximately 0.005 inch, and total coating thickness after siliciding at approximately 0.008 inch. Evaluation tests included in the program were cyclic furnace oxidation at 1600 and 2400° F followed by bend testing; ballistic impact at room temperature and 1600° F, followed by oxidation testing at 1600 and 2400° F; mechanical property tests at room temperature before and after 800 hours of furnace cyclic oxidation exposure at 2400° F; oxidation-erosion testing in a Mach 0.85 rig operated on JP-5 fuel and air; and slow-cycle testing to 2300° F.

The coating systems developed in this program afford the longest cyclic furnace oxidation lives of any coating systems evaluated on tantalum and columbium alloys in the intermediate temperature range of 1600° F to 2400° F. Table I provides a brief summary of the compositions and furnace oxidation lives of the various coatings. Only a few of the cyclic furnace oxidation tests were carried to the 800-hour duration; most were stopped at approximately 200 hours, but not due to oxidation failures. Coatings NS-1, NS-3, NS-4, NS-15 and NS-23 were selected as the best on T222 alloy; coatings NS-1 and NS-4 as the best on FS-85 alloy.

The V + Ti concentration in the W-Mc-V-Ti modifier could be varied from 10 to 30 percent with wide variation in V/Ti ratio and continue to effect excellent substrate oxidation protection. At the 10 percent V + Ti level, less sintering and subsequently less coating reliability was noted. Only a limited sintering study was made, however.

The use of Ni or Pd as sintering aids was evaluated, producing inferior coatings with excessive oxide or glass formation during test at 2400° F. The coating modifier, however, was sintered for 1.5 hours at 2200° F rather than the standard 2760° F temperature. As a result of the reduced sintering temperature, vanadium and titanium were not vaporized prior to siliciding. The coatings, thus, had a significantly different composition than comparable slip compositions sintered at 2760° F for the standard 15-hour cycle.

TABLE I

FURNACE CYCLIC OXIDATION LIVES OF COATED T222 AND FS-85 ALLOYS

Modifier Alloy Designation	Modifier Composition (weight %)					Modifier Composition (atomic %)					Sintering Time (hrs) and Temp. (°F)	Silicon Modifier Atomic Ratio	Maximum Oxidation Lives After Siliciding	
	Mo	W	Ti	V	Other	Mo	W	Ti	V	Other			Hours at 1600°F	Hours at 2400°F
T222 Alloy														
TNV-7[1]	35	35	15	15		31.4	16.4	26.9	25.2		15/2760		> 630	> 1064
TNV-12[1]	95.3		4.7			91		9			15/2760		> 659	947
TNV-13[1]		95	5				83.2	16.8			15/2760		47	> 515
NS- 1	35	35	15	15		31.4	16.4	26.9	25.2		15/2760	2.3	> 237	237
NS- 2	35	35	10	20		31.6	16.4	18.1	34.0		15/2760	2.3	> 214	> 214
NS- 3	35	35	20	10		31.2	16.3	35.7	16.8		15/2760	2.2	> 218	> 808
NS- 4	20	50	15	15		19.7	25.0	28.8	27.1		15/2760	2.0	> 218	> 808
NS- 5	50	20	15	15		42.1	8.8	25.3	23.8		15/2760	2.2	> 218	> 218
NS- 6	40	40	10	10		40.0	21.0	20.1	18.9		15/2760	2.7	> 209	> 209
NS- 7	45	45	5	5		51.2	26.6	11.4	10.7		15/2760	2.3	> 214	> 214
NS- 8	40	40	5	5		40.4	21.1	10.1	28.4		15/2760	2.4	> 218	> 218
NS- 9	42.5	42.5		15		45.7	23.9		30.4		15/2760	2.5	> 218	> 218
NS-10	70	20	5	5		70.1	10.5	10.0	9.4		15/2760	1.9	> 214	> 214
NS-11	33	33	14.2	14.2	5.6 Ni	28.8	15.0	24.8	23.4	8.0 Ni	1.5/2200	3.2	> 218	> 218
NS-12	35	35	14.5	14.5	1 Ni	31.5	16.4	26.0	24.6	1.5 Ni	1.5/2200	3.1	> 218	> 218
NS-13	35	35	14.5	14.5	1 Pd	31.7	16.5	26.2	24.7	0.8 Pd	1.5/2200	3.3	40	> 238
NS-14	15	65	10	10		17.0	38.8	22.8	21.4		15/2760	2.6	> 209	> 209
NS-15	15	65	15	5		16.9	38.4	34.0	10.7		15/2760	2.2	> 209	> 808
NS-16	15	65	15		5 Fe	17.1	38.8	34.3		9.8 Fe	15/2760	2.6	60	> 209
NS-17	28	42	15	15		25.9	20.2	27.8	26.1		15/2760	2.4	> 209	> 209
NS-18	20	50	20	10		19.0	24.8	38.2	17.9		15/2760	2.1	> 209	> 209
NS-19	41.5	41.5	15		2 Fe	43.6	22.9	29.8		3.6 Fe	15/2760	2.8	> 209	> 209
NS-20	42	42.5	15		0.5 B	43.3	22.9	29.2		4.6 B	15/2760	2.3	> 209	> 209
NS-21	68	20	5	5	2 Fe	67.1	10.3	9.9	9.3	3.4 Fe	15/2760	2.2	> 209	> 209
NS-22	69.5	20	5	5	0.5 B	67.0	10.1	9.6	9.0	4.3 B	15/2760	2.2	20	> 209
NS-23	15	63	15	5	2 Fe	16.5	36.2	33.2	10.4	3.8 Fe	15/2760	2.2	> 209	> 808
NS-24	15	64.5	15	5	0.5 B	16.4	35.8	32.8	10.2	4.8 B	15/2760	2.3	2	> 209
NS-3Fe	35	35	20		10 Fe	31.7	16.5	36.3		15.5 Fe	15/2760	2.5	80	> 209
NS-10Fe	70	20	5		5 Fe	70.7	10.5	10.1		8.7 Fe	15/2760	2.1	> 209	> 209
FS-85 Alloy														
NS- 1		See above					See above				15/2760	2.3	> 209	> 800
NS- 3											15/2760	2.2	> 209	> 209
NS- 4											15/2760	2.3	> 209	> 800
NS-15											15/2760	2.2	> 209	> 209
NS-23											15/2760	2.2	121	> 209

(1) Reference 1 coatings

Attempts to substitute iron for vanadium confirmed the necessity of retaining vanadium in the coatings to prevent low-temperature oxidation failures. Increasing the tungsten content at expense of molybdenum increased the severity of the low-temperature oxidation problem in vanadium-free coatings. The iron was observed to improve coating sintering while leaving the coating essentially free of this element if sintered at 2760° F.

The addition of boron to the modifier showed no improvement in 1600° F oxidation life when the modifier was sintered in vacuum for 15 hours at 2760° F.

While the principal evaluation of the coatings was conducted using the T222 alloy, selected coatings were tested for their ability to protect the columbium-base alloy FS-85. The results were similar with the exception that greater coating-substrate interdiffusion and bonding occurred with the FS-85 alloy. As a result of this increased interdiffusion, higher concentrations of titanium were retained in the substrate than with the T222 alloy. Similar modifier compositions could, therefore, be expected to provide slightly different composition coatings on tantalum and columbium alloys.

Bend tests showed that significant ductility was retained by all of the coated alloys after exposure for 200 hours at either 1600 or 2400° F in an oxidizing environment. Of all specimens evaluated, only one coated specimen failed when subjected to a room temperature 1T 90 degree bend after the 200-hour exposure at 2400° F.

Ballistic impact testing was conducted at two moderate impact levels and at both room temperature and 1600° F. Post oxidation testing was performed at 1600° F and at 2400° F. Room temperature damage was less severe than 1600° F damage as judged by oxidation testing and coated FS-85 was less sensitive to impact damage than T222. Many severely damaged specimens of both coated alloys withstood 10 to 20 hours of cyclic oxidation testing after impact. The lower temperature (1600° F) produced the most severe oxidation failures. Coatings containing greater than 25 atomic percent titanium were the only ones to survive more than two hours at 1600° F after being impacted at 1600° F. This improved performance appears to be due to improved sintering and possibly to titanium-substrate alloying. For coatings containing vanadium and titanium, the impact life was apparently enhanced by the addition of iron which increased modifier density by improved sintering.

Mechanical property tests revealed that considerable ductility was retained in the substrate when coated with the NS-series silicides both before and after oxidation. The strength of the substrate was reduced somewhat in the coating process with slight additional loss during 800 hours of 2400° F oxidation testing. The ultimate strength reduction for the 0.030 inch thick substrate was, however, only approximately 20 percent, which could be almost completely accounted for by the silicon penetration into the substrate.

The majority of the coatings performed exceptionally well in oxidation-erosion tests at T_{max} of 2400° F. The NS-4 composition on T222, sintered at 3100° F, silicided to produce the most outstanding coating with both of the tested erosion bars surviving more than 200, one-hour cycles to 2400° F. At the end of this period, the wedge area appeared to be in excellent condition, but testing was discontinued due to shank and radius deterioration.

On the FS-85 alloy, composition NS-1 and -4 modifiers produced coatings that performed well in oxidation-erosion at 2400° F with all specimens surviving more than 150 hours each in test. These tests, as with the T222 coated specimens, were not terminated as a result of failure in the hot wedge area but rather in the cooler tip or radius areas on the specimens.

The investigation of process variables revealed that oxygen content in the modifier metal powders must be maintained at a maximum level of 0.2 percent to produce satisfactory coatings. It was also noted in the program that titanium hydride was a far more satisfactory addition to the coatings than titanium metal; titanium hydride also contained considerably less oxygen.

The sintering temperature influenced not only coating density and bonding, but also composition. The coatings sintered at 2200° F lost virtually none of the sintering aids (Ni or Pd), V, or Ti. Coatings sintered at 2760° F lost all iron additions and a significant part of the V and Ti with the loss increasing rapidly with increasing sintering temperature. The addition of 2% Fe to form the NS-23 composition (Table I) produced an iron-free coating after a 15-hour, 2760° F sinter and a coating structure similar to the NS-4 after a 15-hour 3100° F sinter, indicating that iron may be a means of providing a dense modifier layer without extremely high sintering temperatures.

Particle size evaluation revealed that, to provide adequate coating uniformity for oxidation protection, it was essential that the average particle size for elemental powders be 3 microns or less. Coatings prepared using pre-alloyed powders could have a particle size as large as 12 microns and retain adequate oxidation protection.

The evaluation of dip coating of hollow vane configurations showed that, by proper design, the vane could be readily coated. Protection never reached the same level as for sprayed coatings but, with equivalent development effort on dipping, it is believed that comparable protection could be afforded by a coating with the modifier applied by dipping. The problem with dipping was the inability to achieve fully sintered and bonded internal surfaces, particularly at the internal trailing edge of the simulated vane geometries.

Because of the mode of failure of erosion bar specimens both in this program and at the NASA/Lewis Research Center, it must be tentatively concluded that additional sintering, modifier, and/or sublayer coating effort is required to achieve fully satisfactory 1200° F to 1600° F protection for these silicide coating systems.

3

THE EXPERIMENTAL PROGRAM

In the experimental program an initial series of ten coating modifier compositions derived from the (35Mo35W15Ta15V)-Si composition were screened through a series of tests in order to provide direction for subsequent, more extensive coating modifications. Approximately 20 additional coatings were then formulated based on trends observed in the initial series. These coatings also examined the effect of activated sintering, liquid phase sintering, pre-alloying of the modifier, particle size, and oxygen content in the modifier powder. The atomic ratio between modifier and silicon and pore volume of the coating was evaluated in detail on many of the coatings. Application of the modifier by spraying and silicon by pack deposition was standard, but dipping techniques and variation in trailing edge geometry were investigated to adapt the process to hollow vanes.

Selected compositions applied to FS-85 and T222 alloys were furnace oxidation tested for 800 hours followed by mechanical property measurements, tested under slow thermal cycles, and tested in an oxidation-erosion rig at 2400° F.

3.1 MATERIALS AND APPLICATION TECHNIQUES

3.1.1 Materials

Substrate Materials

The 0.060-inch T222 tantalum alloy utilized for cyclic oxidation tests was that remaining from Contract NAS3-7276 and described in Reference 1. The hollow airfoils used in dipping experiments were fabricated from 0.030-inch stainless steel, Cb-1Zr and T222. The ingot chemical analyses of the T222 (Heat No. 91031) supplied by the Wah Chang Corporation is shown in Table II.

The 0.500-inch diameter T222 rods (Heat No. 650047 and 65070) and 0.250-inch by 1-inch bars (Heat No. 650047) for erosion bars were obtained from Wah Chang. The chemical analyses are shown in Table II. The 0.030-inch, 0.060-inch, and 0.25-inch FS-85 alloy was supplied to the Solar specification (Appendix A) by Fansteel. Typical ingot analyses are shown in Table III for Lot Numbers 85D1560 and 85D1682, respectively. The 0.500-inch diameter FS-85 rod, used for erosion bars, was produced by Wah Chang Corporation, Heat Number 91048 (Table III).

TABLE II

INGOT ANALYSIS OF T222 ALLOY (Ta-9.6W-2.4Hf-0.01C)

Heat No.	Ingot Analysis									Product Hardness	
	W (wt %)	Hf (wt %)	Cb (ppm)	Ti (ppm)	Fe (ppm)	O (ppm)	N (ppm)	C (ppm)	H (ppm)	BHN	DPH
91031	9.1	2.05	<300	<20	25	100	30	<120	2.8	229-285	240-304
650047	10.2	2.6	380	<20	<20	70	15	110	2.3	285-302	304-315
65070	10.3	2.6	800	<20	35	<50	<45	105	2.3	255-269	265-266

TABLE III

INGOT ANALYSIS OF FS-85 ALLOY (Cb-11W-28Ta-1Zr)

Heat No.	Ingot Analysis									Product Hardness
	Ta (wt %)	W (wt %)	Zr (wt %)	Fe (ppm)	Si (ppm)	C (ppm)	O (ppm)	N (ppm)	H (ppm)	BHN
91048	27.5	10.5	0.92	< 50	< 50	40	100	22	5	179-201
85D1682	26.9	10.5	0.94	50	50	10	140	65	10	
85D1560	26.5	10.5	0.90	50	50	40	75	70		

Coating Materials

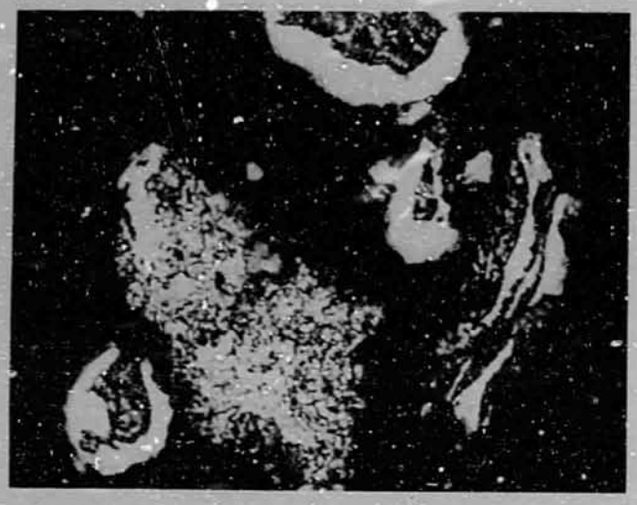
Typical analyses of the molybdenum, tungsten (both 5 microns and 0.7 micron - 5-micron powder was standard throughout the program; the finer tungsten powder is noted where used) and titanium powders, together with titanium and vanadium sponge, are shown in Table IV. Both vanadium and titanium sponge were converted to the respective hydrides before incorporation into the coatings. The vanadium was first hydrided and then reduced to -325 mesh powder by ball milling with a high alumina mill and balls (U.S. Stoneware, Burundum). Hydriding produced a product with an oxygen content less than 0.5 percent except for the initial high oxygen content lot which was inadvertently contaminated to contain ~4 percent oxygen. (Hydriding procedures are described in Appendix B.) The initial coatings were prepared using titanium metal powder (Table IV) from Metals Disintegrating Corporation, but the majority of the coatings had titanium added as the hydride. The titanium hydride was prepared by reacting the metal sponge, characterized in Table IV, using the procedure described in Appendix B. During hydriding, the oxygen content of the titanium remained unchanged within the analytical uncertainty; the oxygen content was 600 ± 40 ppm.

TABLE IV

COATING MATERIALS

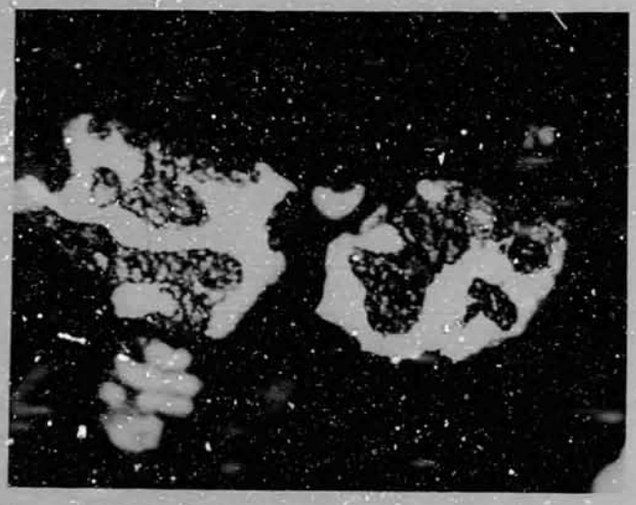
Material	Vendor	Particle Size	Chemical Element (ppm or %)																
			Si	Fe	Cr	Ni	Cu	Mn	Mg	Sn	Mo	Na	K	Ti	C	N	O	H	W	V
Tungsten	General Electric Lamp Metals and Components Dept.	4.50μ	8	7	<3	3	<3	<6	3	<6	125	5	14	-	<10	-	170	-	-	-
Tungsten	General Electric Lamp Metals and Components Dept.	0.74μ	<7	33	6	13	3	<6	4	<6	135	38	88	-	16	-	2460	-	-	-
Molybdenum	General Electric Lamp Metals and Components Dept.	5.20μ	<15	<15	<8	<5	<4	<10	<10	12	-	-	-	-	<10	-	610	-	88	-
Titanium	Oremet	Sponge -20 + 40 mesh	-	200	-	-	-	-	-	-	-	-	-	-	200	70	590	30	-	-
Titanium	Metals Disintegrating Corporation MD 301	-325 mesh	-	560	-	-	-	-	-	-	-	-	-	-	430	230	3100	-	-	-
Vanadium	Vanadium Corporation of America	Sponge -1 + .5 mesh	-	300	-	-	-	-	-	-	-	-	-	-	400	300	900	50	-	-
Pre-alloyed	Wah Chang Albany, Oregon	-325 mesh	50	150	<5	10	100	50	5	25	36.1%	-	-	14.7%	250	335	1400	18	35.2%	15.07%

The pre-alloyed material of NS-1 composition was obtained from the Wah Chang Corporation. The material was the product of arc melting the respective elements together and crushing the resultant ingots to -325 mesh in an argon atmosphere. An analysis of the powdered alloy is shown in Table IV. The alloy, as shown by data, corresponds closely to the nominal composition of NS-1 (35Mo35W15Ti15V). The total of the analytical percentages of the four main elements is 101.07. This suggests experimental uncertainty in the order of 0.5 to 1.0 percent for one or more of the four main elements. Figure 1 shows the microstructure of different particles (-325 mesh), and reveals considerable variation in the size, shape and degree of homogeneity for the different particles. The density of the pre-alloyed powder was measured at Solar by the Pycnometric technique and was 9.22 ± 0.08 g/cm^3 at 24°C (75° F). The Fisher subsieve particle size of the as-received powder was 13.4 microns.



Murakami Etchant

Magnification: 750X



Murakami Etchant

Magnification: 750X

FIGURE 1. PRE-ALLOYED NS-1 ALLOY POWDER

The -200 mesh silicon used in the pack siliciding operations was obtained from Keokuk Electro-Metals Company as Lot Number 3991. The impurity analysis yielded 0.33 percent iron, 0.04 percent calcium, and 0.21 percent aluminum.

The powdered elemental materials or pre-alloyed powders were normally ball milled for 20 hours in the E-4 vehicle (App. C) using Burundum balls and mill jars. A liquid to solid ratio of 2.5/1 by volume was used. The slurries were stored in small glass jars purged with argon prior to sealing.

3.1.2 Application Techniques

Preparation of Specimens

The standard oxidation specimens were prepared by shearing the substrate alloy into 1-inch by 2-inch pieces, tumbling in an abrasive compound until all edges and corners were uniformly rounded, sandblasting with 80 grit garnet, and etching in $45HNO_3$-$45H_2SO_4$-10HF. Water and acetone rinses preceded drying, weighing, and measuring of the specimens. The mechanical test specimens (Sec. 3.4.3), thermal cycling specimens (Sec. 3.4.4), erosion bars (Sec. 3.4.5), and the hollow vanes (Sec. 3.7.2) were prepared for coating in the same manner as above for all operations following shearing.

Modifier Spray Application

The slurries were sprayed on the specimens by hand operations using a Model TGA-Series 501 DeVilbiss spray gun with and "F" tip. Following air drying, the specimens were supported on tungsten rods and sintered in vacuum (10^{-5} to 10^{-6} Torr), usually for 15 hours at 2760° F. Specific details of the holding fixture, firing racks, and firing procedure are provided in Reference 1. A detailed discussion of the applications of the modifier by dip coating is found in Section 3.7.2.

Siliciding

After sintering, the specimens were weighed, packed in pure -200 mesh silicon (no halide activator added) and silicided for 15 hours at 2150° F in argon (800 Torr). The specimens were measured and re-weighed after siliciding. The details of pack configuration and equipment are covered in Reference 1.

3.2 COMPOSITION OF COATINGS

The most outstanding coating at the outset of this program was the Solar-NASA coating TNV-7 (35Mo35W15Ti15V)-Si (Ref. 1). This coating had demonstrated long-term (>600 hours) oxidation protection to T222 alloy at both 1600° F and 2400° F

with a potential of meeting the multiple thousand hour engine operation objective. Essentially all coatings investigated in this program are an outgrowth of this composition.

Process conditions were kept as constant as possible for parameters that had proven satisfactory in the previous program. This included vehicle, particle size, coating thickness, and sintering time and temperature. Siliciding of the basic chemistries was accomplished by unactivated high-pressure pack cementation. The silicon deposition was retained constant at a silicon to modifier atomic ratio of 2 to 2.5:1 based on the modifier slip composition. Because of the good performance of the coatings in cyclic furnace evaluation in the previous program, the major effort of this program was directed toward optimization of coating composition.

The 35Mo35W15Ti15V chemistry was altered by five component concentration variations which resulted in ten modifier chemistries, as described in Series I. The evaluations of iron as a substitute for vanadium in three modifiers together with three modifiers using Ni or Pd as sintering aids are described in Series II. The high W/Mo ratio observed to be beneficial in NS-4 was further investigated with three variations giving four modifier chemistries described as Series III. (The attempts to substitute iron for vanadium produced coatings which exhibited superior resistance to impact damage. These same coatings, however, performed poorly in 1600° F oxidation.) In an attempt to improve coating impact resistance while retaining good 1600° F oxidation protection, further evaluation was conducted based on the addition of Fe or B to three coatings retaining vanadium to produce six new modifier chemistries described in Series IV.

3.2.1 Series I - NS-1 to NS-10

The technical basis for the selection of the modifier elements is discussed in detail in Reference 1. The evaluation of the coatings in that reference revealed the outstanding performance of TNV-7 (35Mo35W15Ti15V). From the technical basis, it is pointed out that the oxidation resistance of titanium disilicide is not as good as that of either WSi_2 or $MoSi_2$ at 2400° F; however titanium enhances the oxidation resistance of tantalum in the absence of silicon (Ref. 2 and 3). Oxidation tests performed at Solar at 2400° F showed that Ti/W and Ti/Mo silicides in bulk form had very good oxidation resistance (Ref. 4) and served as promising coatings for titanium (Ref. 1). The oxidation resistance of vanadium disilicide was observed to be particularly good at lower temperatures exhibiting no pest-type failure at 1500° F (Ref. 4) in contrast to the failures observed for WSi_2, $MoSi_2$, and $TaSi_2$.

The TNV-7 modifier designated NS-1 for the series was changed to produce nine diffused modifier chemistries, described in Table V. The evaluation of these chemistries was conducted to further optimize the NS-1 composition.

TABLE V

COMPOSITIONAL VARIATIONS OF NS-1 TO BE EVALUATED FOR CHEMISTRY OPTIMIZATION: SERIES I

Composition	Approach for Modification
NS-1 35Mo35W15Ti15V	Basic starting chemistry
NS-2 35Mo35W20Ti10V NS-3 35Mo35W10Ti20V	Retain Mo/W ratio, change Ti/V ratio
NS-4 20Mo50W15Ti15V NS-5 50Mo20W15Ti15V	Retain Ti/V ratio, change Mo/W ratio
NS-6 40Mo40W10Ti10V NS-7 45Mo45W5Ti5V	Retain Mo/W and Ti/V ratios, but reduce Ti-V content
NS-8 40Mo40W5Ti15V NS-9 42.5Mo42.5W15V	Retain Mo/W ratio and V content, but lower Ti
NS-10 70Mo20W5Ti5V	Retain Ti/V ratio, reduce Ti-V content and increase Mo/W ratio

The initial slurries were prepared as described in Appendix C utilizing Mo, W and Ti powders described in Section 3.1.1, milled with vanadium from a new lot of vanadium hydride powder. Early oxidation failure (<16 hours at 1600° F) of specimens coated with this slip led to the investigation of several possible causes including the effects of oxygen content in the elemental powders. These evaluations are covered in detail in Section 3.5.3 showing detrimental effects of high oxygen content materials to oxidation performance. A new lot of low oxygen content (<.5% oxygen) vanadium hydride was prepared. This material, when used with the other powders, provided slip that produced oxidation resistant coatings protecting T222 alloy for 200 hours at either 1600 or 2400° F. A portion of the initial ten modifier chemistries and all subsequent coatings included titanium as TiH_2, which also was observed to improve oxidation protection over the use of elemental powder.

The slurries were sprayed on the specimens, sintered, and silicided as described in Section 3.1.2.

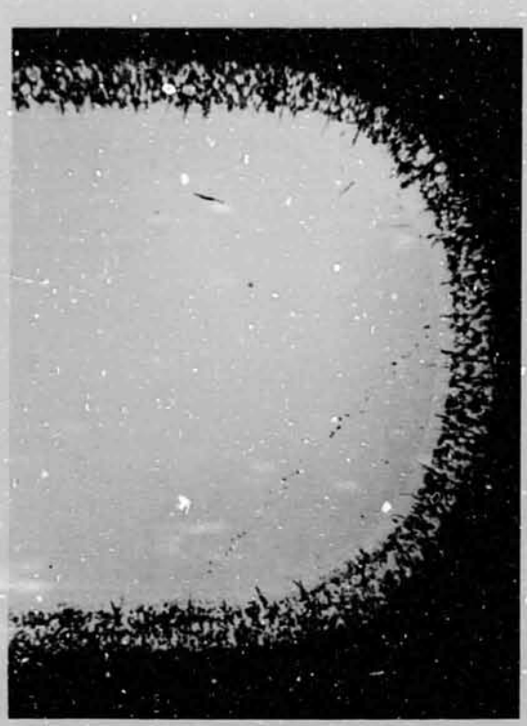
Each of the ten modifier alloys in Table V was applied to the T222 alloy. The thicknesses ranged from 0.004 inch to 0.006 inch. Coating weights ranged from 50 to 90 mg/cm^2. Although influenced by thickness control, weight variation depended significantly on the average density of the modifier alloys. After siliciding, the

additional gain in thicknesses and weights ranged from 0.303 inch to 0.005 inch and 35 to 55 mg/cm^2, respectively.

The microstructures of the NS-1 to NS-10 as silicided coatings had certain similarities. Typical examples are shown in Figures 2 through 7. Significant porosity is apparent in each of the coatings. In all cases the silicon has penetrated through the porous sintered coating and into the substrate. Examination of the photomicrographs taken at 40X magnification reveals that the thickness of the sintered coatings and the silicided sublayer varies with location on the specimens. Despite this lack of uniformity (resulting from the hand-spraying process), none of the specimens prepared in the experiments for which the metallography is shown in Figures 3, 4, 5 and 8 were observed to fail in the oxidation test periods of 200 hours at either 1600 or 2400° F. A diffusion zone is apparent in Figures 2, 3, 4, and 5 between the silicide and the unaffected substrate. This zone is attributed to titanium from the modifier diffusing into the substrate alloy. In contrast, the modifier alloys NS-9, which is titanium-free (Fig. 8) and NS-7, which is only 5 percent Ti (Fig. 6 and 7), show no metallographically visible modifier/substrate diffusion zone. (Note! All metallographic specimens in the program were etched in 15 lactic acid, 5 hydrochloric acid, and 5 nitric acid unless figures note otherwise.)

The silicided layer was observed to contain a multiplicity of phases (which are partially characterized in Sec. 3.4.2). The light-colored nonporous zone located within the substrate was shown by electron microprobe analysis to result from converting the substrate to the disilicide. Regardless of the variation in composition (varying from 30%(V + Ti) for NS-1 and NS-4 to 15%V for NS-9), the porosity in the protective coatings in the as-silicided condition is quite consistent as shown in Figures 3, 4, 5, 7, and 8. Greater variations in percent porosity were observed from run to run for the same coating (Fig. 2 and 3 for NS-1 and Fig. 6 and 7 for NS-7) than the variations that could be related to change in composition.

Three runs of NS-1 are shown in Figures 2, 3, and 4. Figure 2 shows the high porosity (16 percent surface connected pores as determined by the technique described in the following section) retained in the silicided coating prepared from slip using vanadium hydride containing < 0.5 percent oxygen and titanium added as hydride. All samples coated using the lower oxygen content modifier survived >200 hours oxidation at both 1600 and 2400° F. Figure 4 shows the low porosity (8 percent surface connected), but significantly coarser structure of the coating prepared using pre-alloyed modifier applied as 12 micron powder (average) rather than the 2-micron particles of elemental powder for the coating shown in Figure 3. The pre-alloyed coating shown in Figure 4 performed equally as well in oxidation tests as the elemental powder coating shown in Figure 3. The coatings shown in Figures 6 and 7 are both NS-7 (45Mo45W5Ti5V). The significant difference is the reduced porosity in Figure 7 (7 percent surface connected) as compared to Figure 6 (15 percent surface connected). The only variable between the two coatings was the substitution of titanium hydride for powdered elemental titanium. (The titanium hydride produced the lower porosity.)



EDGE VIEW

Magnification: 40X

FLAT AREA

Silicide of Modifier Alloy

KHN
(50 gm Load)

Silicide of Diffusion Zone Between Modifier and T222 Alloy

430

406

Titanium-Rich Diffusion Zone

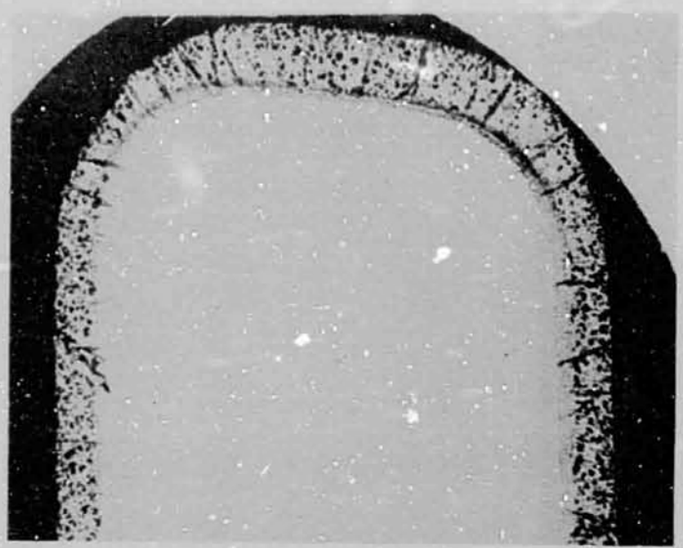
319

343

Magnification: 250X

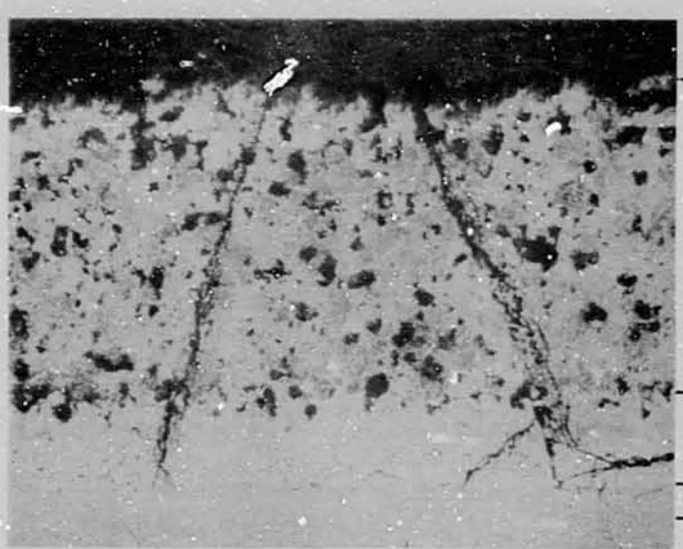
GL 325-343

FIGURE 2. SILICIDED NS-1 COATING PREPARED USING HIGH OXYGEN CONTENT (1-4%O_2) VANADIUM



EDGE VIEW

Magnification: 40X



FLAT AREA

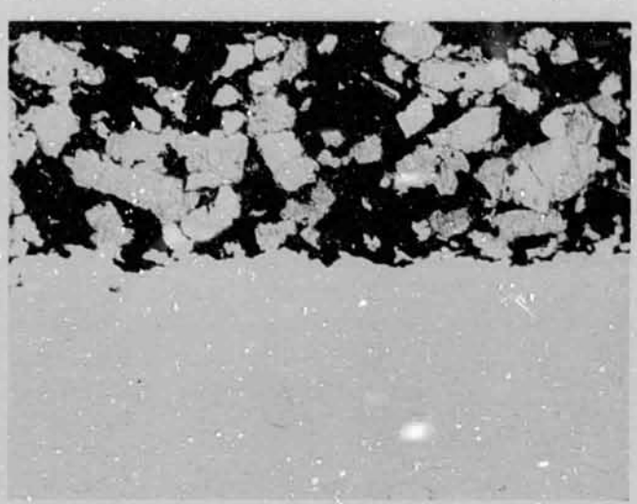
Silicide of Modifier Alloy

Silicide of Diffusion Zone Between Modifier and T222 Alloy

Titanium-Rich Diffusion Zone

Magnification: 250X

FIGURE 3. TYPICAL NS-1 COATING AFTER SILICIDING



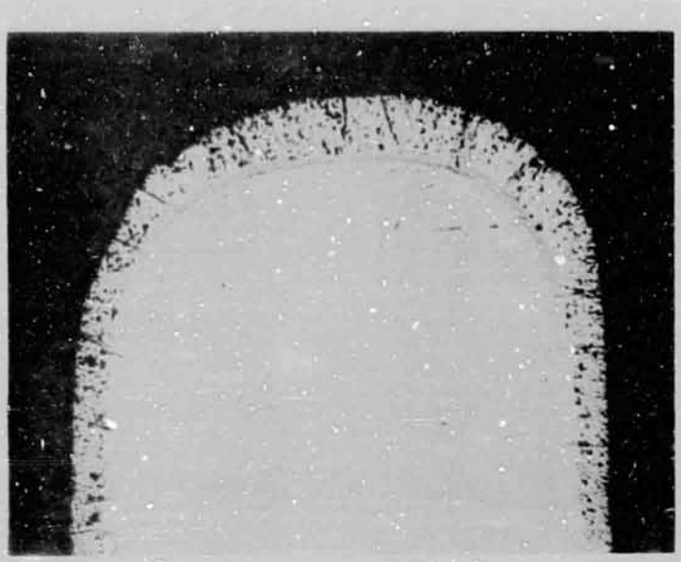
As-Sintered

Magnification: 250X

As-Silicided

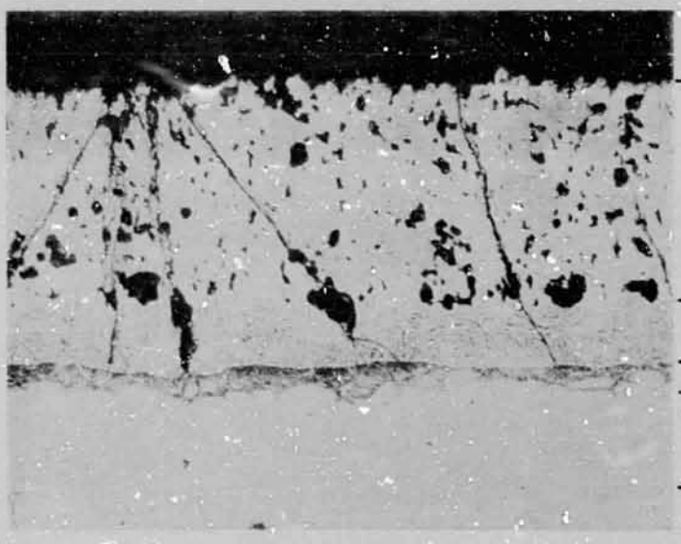
Magnification: 250X

FIGURE 4. SINTERED AND SILICIDED PRE-ALLOYED NS-1 MODIFIER



EDGE VIEW

Magnification: 40X



FLAT AREA

Silicide of Modifier Alloy

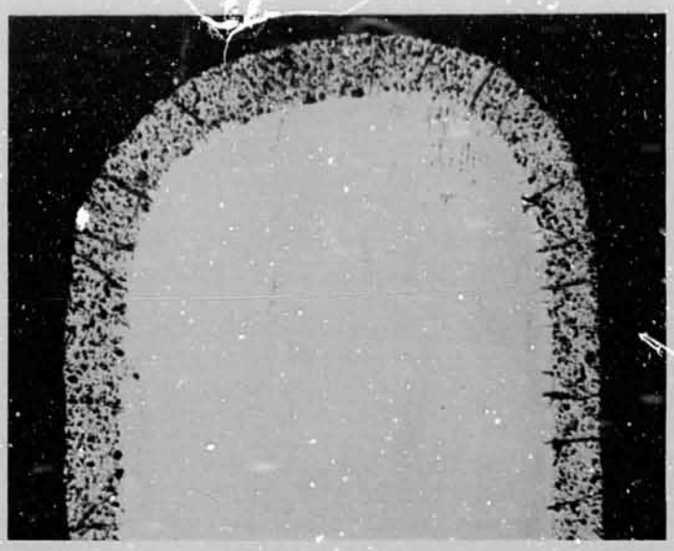
Silicide of Diffusion Zone
Between Modifier and T222 Alloy

Titanium Rich Diffusion Zone

T222 Alloy

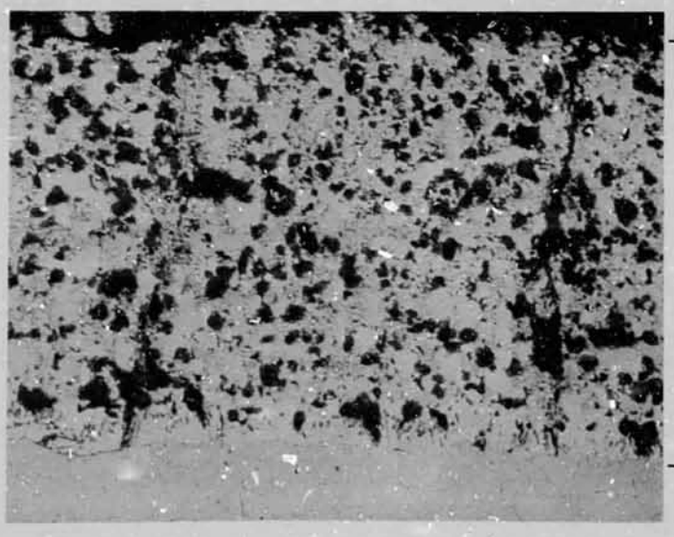
Magnification: 250X

FIGURE 5. NS-4 COATING AFTER SILICIDING



EDGE VIEW

Magnification: 40X

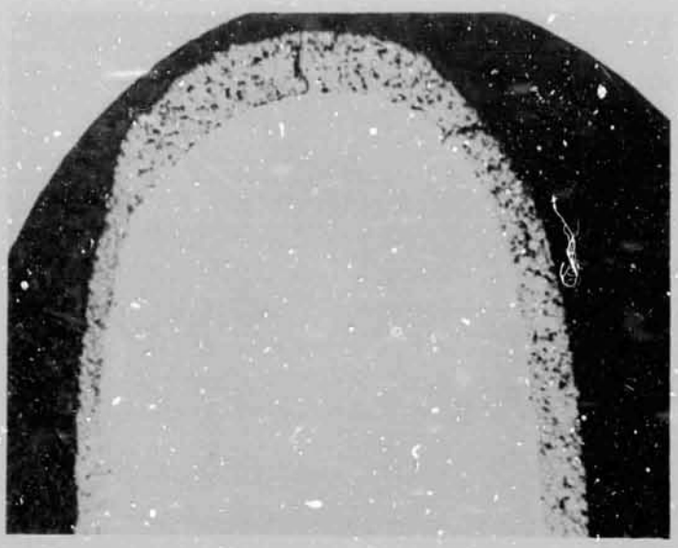


FLAT AREA

Silicide of Modifier Alloy

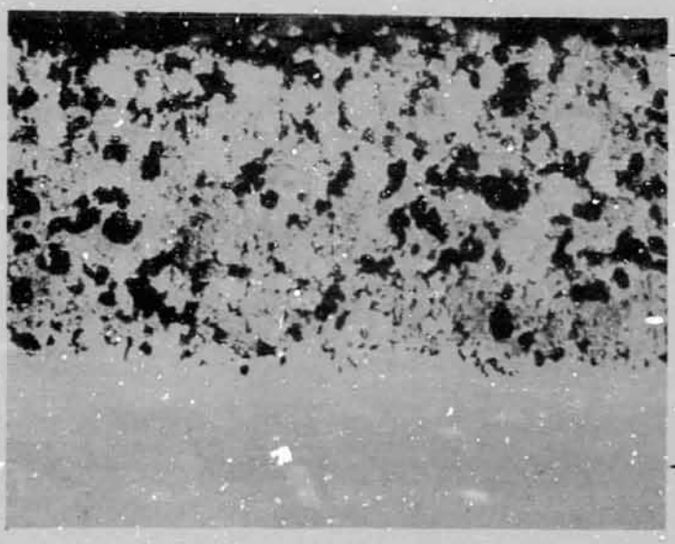
Magnification: 250X

FIGURE 6. SILICIDED NS-7 COATING PREPARED USING TITANIUM POWDER



EDGE VIEW

Magnification: 40X

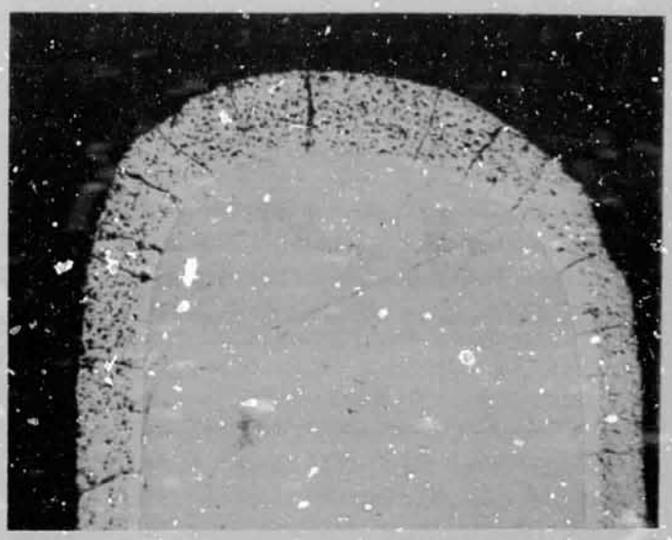


FLAT AREA

Silicide of Modifier Alloys

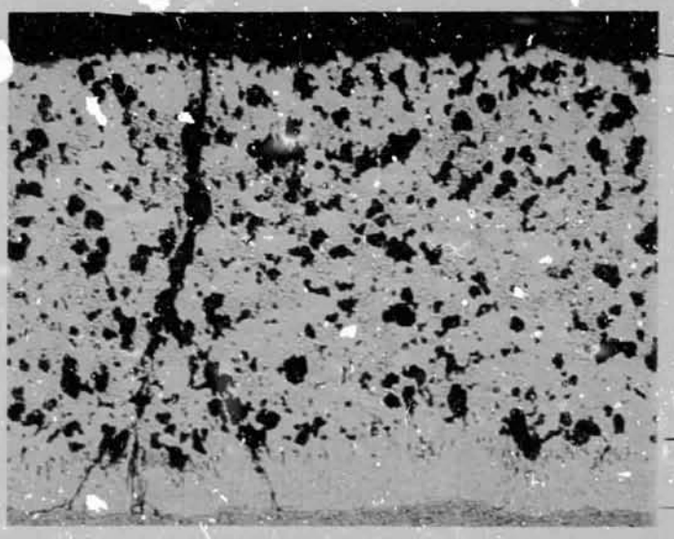
Magnification: 250X

FIGURE 7. SILICIDED NS-7 COATING PREPARED USING HYDRIDED TITANIUM



EDGE VIEW

Magnification: 40X



FLAT AREA

Silicide of Modifier Alloy

Silicide of Substrate

Magnification: 250X

FIGURE 8. THE NS-9 COATING AFTER SILICIDING

Evaluation of Surface Connected Coating Porosity

To provide greater insight into the influence of the various modifier constituents on the porosity of the coatings as well as determine the relationship of porosity to coating performance, the surface connected pore volume was measured at three stages: as-sintered, as-silicided, and as-tested for 200 hours at 2400° F.

The technique used for pore volume measurement consisted of the following steps:

- Micrometer measurement of coating thickness and area and calculation of coating volume (0.063-inch by 1-inch by 2-inch specimens were standard).
- Weighing the specimen
- Removal of air from pores by vacuum outgassing at an absolute pressure of 0.1 Torr
- Immersion in DC704 silicone liquid (density 1.067 gm/cc) while under the 0.1 Torr pressure
- Increasing the pressure to 760 Torr
- Removing the specimen from the liquid and wiping with a liquid saturated blotter to remove all liquid not entrapped in the pores
- Weighing specimen, calculating pore volume from weight differential and determining percent pores

A limited number of pore volume tests were performed on the as-sintered modifier prior to siliciding. The surface connected pores ranged between 45 and 62 volume percent of the first ten chemistries.

Data on pore volume was more extensive for the as-silicided coatings. Some conclusions drawn from the evaluation of the data in correlation with chemistries and oxidation performance are:

- Use of titanium hydride in most coatings results in a considerable decrease in surface connected pores.
- Poor performance in cyclic furnace oxidation at 1600° F appears to correlate with high pore volume in the as-silicided condition

The relationship of 1600° F oxidation life to pore volume in the as-silicided condition is plotted in Figure 9. It shows the consistently good performance associated with <12 percent pore volume as compared to almost certain early failure at >15 percent pore volume. No satisfactory coatings contained less than 8 percent porosity in the as-silicided condition.

Pore volume, after testing for 200 hours at 2400° F, is probably the least significant value determined. Assessing the effect of pore volume on performance is not possible from these results because all specimens remaining for evaluation have already withstood the test conditions. It is interesting to note, however, that the pore volume for all coatings in the as-oxidized, 200 hours at 2400° F, condition varied from 5 to 10 percent. For all coatings on T222, which survived 800 hours at 2400° F, the pore volume was 5 percent. The decrease in pore volume with exposure appears to be due to the growth of surface oxides which seal both general surface connected porosity and cracks in the silicide. As can be seen in Section 3.3.2 (Fig. 26), the surface oxides do not necessarily crack on thermal cycling. The low expansion of the glassy oxide and low softening temperature minimize the thermal stresses developed in this phase.

While pore volume in the as-sintered condition may contribute to silicide pore volume, it does not predetermine pore volume in the silicided product. As an example; coatings such as NS-1 (run number 10) had an as-sintered pore volume of 49 percent (good coatings generally ranged from 45 to 60 percent surface interconnected pores), but silicided to 19 percent pore volume. In contrast, NS-2 (run number 2) had an as-sintered pore volume of 59 percent which silicided to 14 percent surface connected pore volume. Subsequent evaluations of oxidation performance showed the most consistent relationship of oxidation protection to be pore volume in the as-silicided condition.

3.2.2 Series II - Liquid Phase and Activated Sintering

Iron Additions to the Modifier

The evaluation of Series I coatings (Sec. 3.2.1) demonstrated a substantial reduction in 1600° F oxidation protection (failure in <20 hours) for coatings produced from modifiers prepared with high oxygen content (>1 percent oxygen) vanadium hydride (discussed in Sec. 3.5.3). One area of investigation pursued to eliminate the problem was the substitution of iron for vanadium in the modifier. Three coatings, designated NS-3Fe, NS-10Fe, and NS-16, listed in Table VI, were tested to evaluate the effects of the substitution of iron for vanadium in the modifier.

The slurries were prepared as described in Appendix C utilizing Mo, W, and Fe powder milled together with titanium hydride. The modifiers sintered to produce

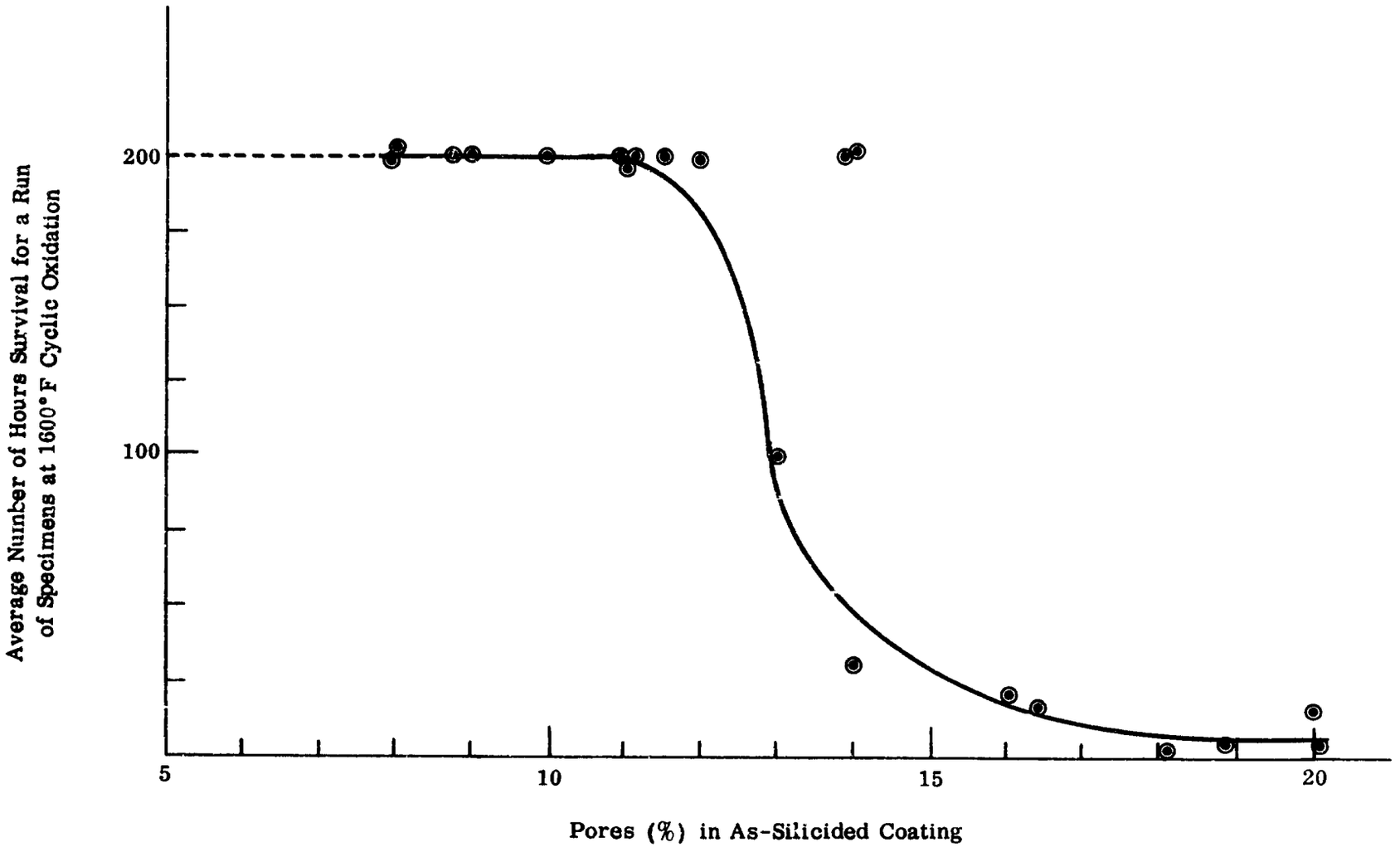


FIGURE 9. THE RELATIONSHIP OF PORE VOLUME TO 1600° F CYCLIC OXIDATION FOR ALL COATINGS WITH MODIFIERS SINTERED AT 2600 TO 2800° F AND WITH SILICON TO MODIFIER ATOMIC RATIO 2 TO 2.8

TABLE VI

MODIFIER COMPOSITIONS WITH SINTERING AIDS: SERIES II

Designation	Composition (wt %)	Change
NS-3Fe	35Mo35W20Ti10Fe	Substitute Fe for V
NS-10Fe	70Mo20W5Ti5Fe	Substitute Fe for V
NS-16	15Mo65W15Ti5Fe	Substitute Fe for V
NS-11	35Mo33W14.2Ti14.2V5.6Ni	NS-1 with sintering aids
NS-12	35Mo35W14.5Ti14.5V1Ni	NS-1 with sintering aids
NS-13	35Mo35W14.5Ti14.5V1Pd	NS-1 with sintering aids

higher density products than the comparable coatings containing vanadium. A typical as-sintered structure is shown in Figure 10. The coating is the iron-containing equivalent to the vanadium-containing coating NS-15 (Sec. 3.2.3). The silicided coatings shown in Figures 10 and 11 had low pore volume:

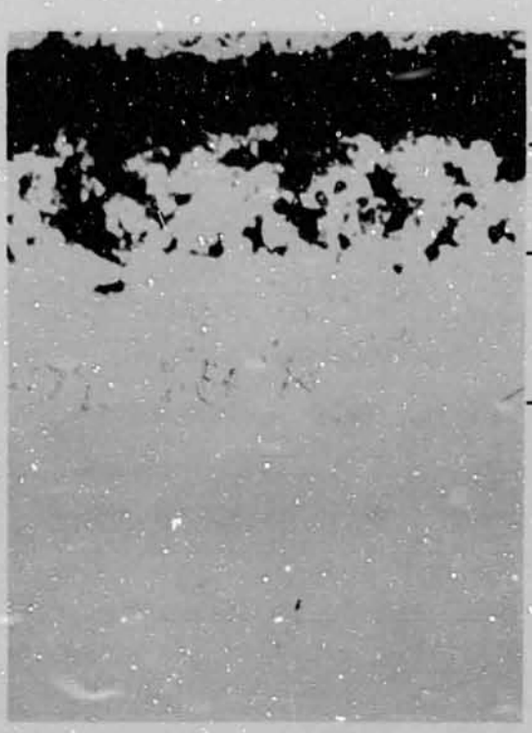
Coating	Pore Volume As-Sintered	As-Silicided
NS-3Fe	---	7%
NS-16	33%	7%

The coatings, however, failed early in 1600° F oxidation tests, as is discussed in Section 3.3.2. Subsequent microprobe analyses revealed that a 15-hour, 2760° F vacuum sinter results in the volatilization of all detectable iron. The resulting W, Mo, Ti silicide coatings developed pest-type failures with coating crystallization accompanied by severe oxide penetration. The time to 1600° F failure was directly related to the molybdenum content in the absence of vanadium, i.e., the higher the Mo, the longer the time to failure.

The NS-16 coating developed less damage on impact than the comparable vanadium-containing coating NS-15, but failed early in test at 1600° F oxidation after impact.

Investigation of Nickel and Palladium Activated Sintering

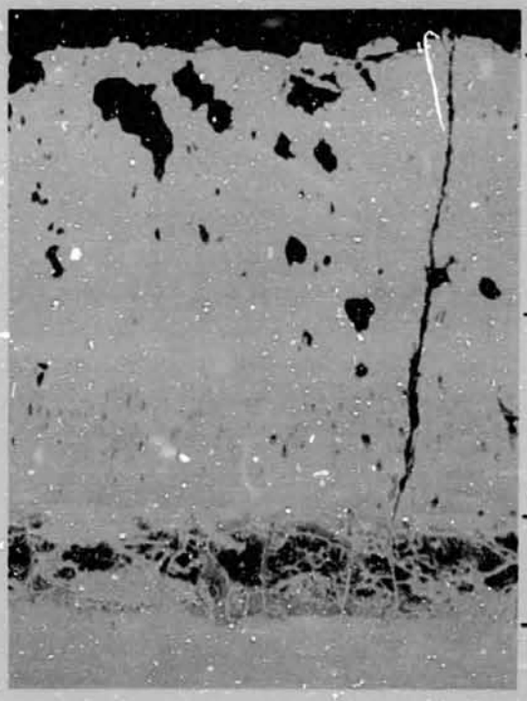
In experiments described in Reference 1, 0.25 percent nickel was added to the 96.5W-2.5Ti modifier alloy, allowing reduction of the 15-hour/2765° F sintering cycle to a 2-1/2-hour/1925° F cycle with improvement of the oxidation resistance.



As-Sintered Modifier Alloy

Diffusion Zone Between Modifier and T222 Alloy

Magnification: 250X



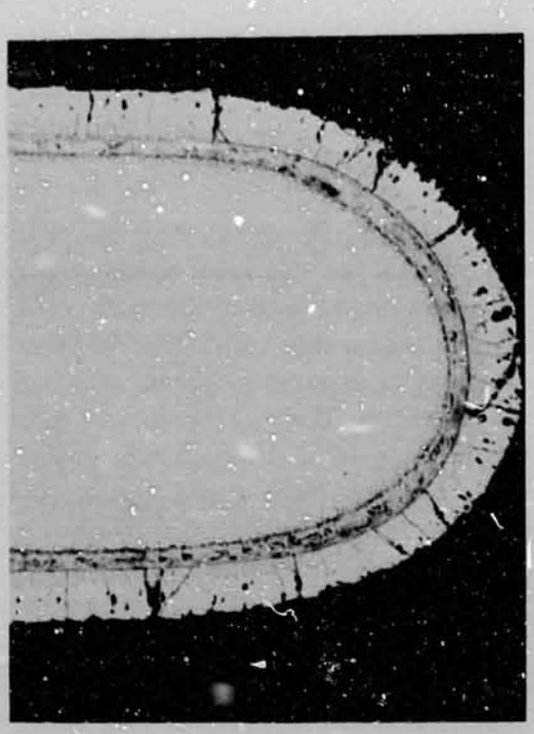
As-Silicided
Silicide of Modifier Alloy

Silicide of Diffusion Zone Between Modifier and T222 Alloy

Titanium-Rich Diffusion Zone

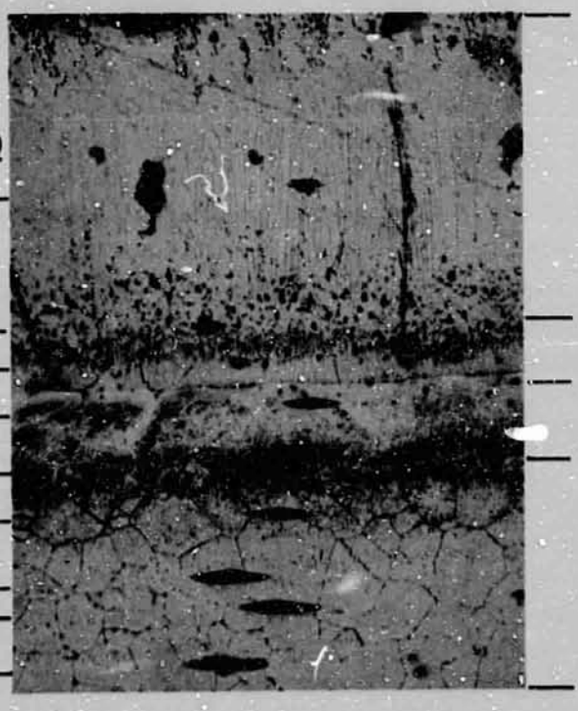
Magnification: 250X

FIGURE 10. NS-16 MODIFIER AS SINTERED AND AS SILICIDED



EDGE VIEW

Magnification: 40X



FLAT AREA

KHN
(50 gm Load)

1435 — Silicide of Modifier Alloy

2055 — Silicide of Diffusion Zone Between Modifier and T222 Alloy

2900 —

643 — Titanium-Rich Diffusion Zone

557 —

530 — T222 Alloy

355 —

312 —

306 — Magnification: 250X

℄ 322

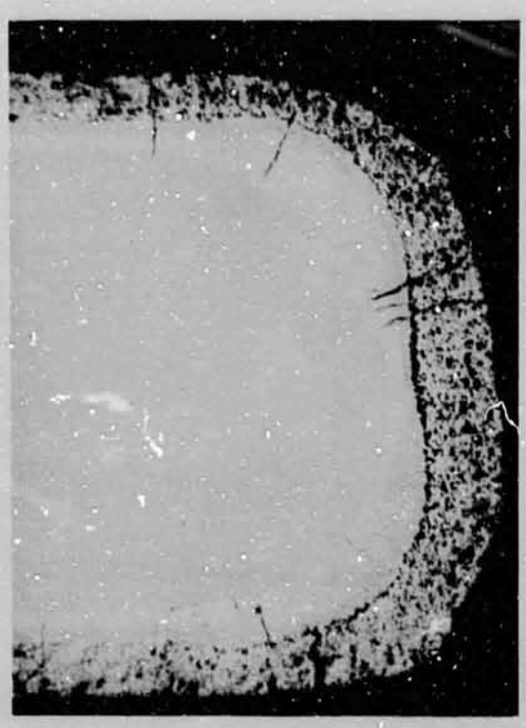
FIGURE 11. NS-3Fe MODIFIER AFTER SILICIDING

In the present program, the addition of 1 percent (NS-12) and 5.6 percent (NS-11) nickel powder to the NS-1 modifier alloy was investigated (Table VI). The 5.6 percent nickel addition corresponds to the amount of nickel required to form the Ti-28.5Ni eutectic alloy with titanium in the NS-1 alloy. This assures liquid phase sintering at 2200° F.

After sintering for 1.5 hours at 2200° F, the specimens were pack-silicided for the standard cycle of 15 hours at 2150° F. The siliciding cycle produced an average weight increase of 65 mg/cm^2 and thickness increase of 0.006 inch. The coatings, although excessively silicided (silicon/modifier atomic ratio>3), had the low surface interconnected pore volume (~9 percent) which appears to be essential for 200-hour cyclic oxidation protection. The microstructure of NS-12 (1 percent nickel), Figure 12, shows the presence of a thick, light colored layer of silicided substrate. Of the two coatings containing nickel, the one containing 1 percent nickel was more resistant to oxidation (the first failure at either 1600 or 2400° F occurred at 218 hours), but the glass formation on the surface of the specimens oxidized at 2400° F was so excessive as to make both coatings poor candidates for use in a high-velocity environment.

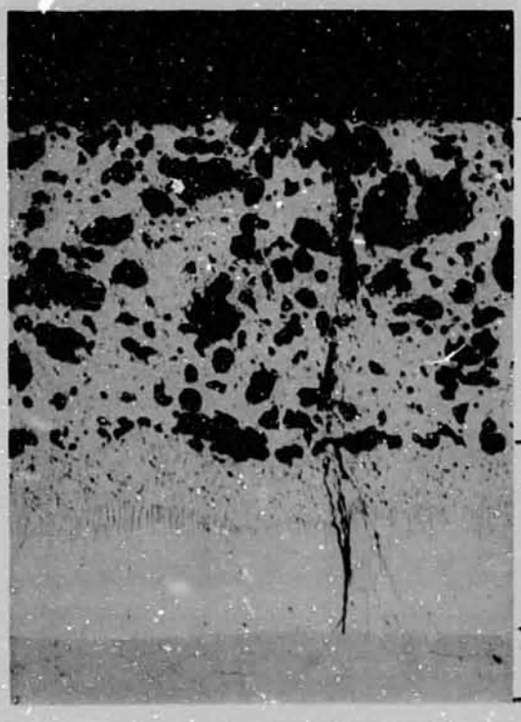
The NS-13 modifier alloy (35Mo35W14.5Ti14.5Pd) was prepared as a modification of the NS-1 alloy by addition of 1 percent palladium. Tungsten (0.74-micron) and molybdenum (5-micron) powders were slurried with an HCl solution of $PdCl_2$. The resultant $PdCl_2$ coated powder was dried and then reduced with hydrogen to produce Pd-coated W and Mo powders. This powder was ball milled with titanium and vanadium hydride powders in the E-4 vehicle to produce the NS-13 modifier alloy. After spraying and drying, the coated specimens were sintered at 2200° F for one and one-half hours. Although the pack siliciding process was cut back from 15 to 12 hours, a weight gain of 72 mg/cm^2 was observed. This was much greater than expected considering the work with the nickel-sintered coatings. Pore volume was 9.6 percent or well within the range that usually withstood 1600° F oxidation testing. The microstructure of the NS-13 coating in the as-silicided condition is shown in Figure 13. This coating, similar to NS-11 and NS-12, showed excessive silicon penetration into the substrate. Oxidation of the coated specimens at 1600° F resulted in three failures at 40 hours. In addition, excessive glass formation was observed in oxidation at 2400° F.

In an effort to understand the cause of excessive glass formation, an X-ray fluorescence analysis was performed and the results are shown in Table VII. The major difference in composition between the surface layers on the two oxidized coatings was in the titanium, vanadium and silicon counts. The surface of the oxidized NS-13 coating, in relation to the oxidized NS-1 coating, was much higher in titanium and vanadium and much lower in silicon. The reduced temperature and sintering time employed with the NS-13 coating (1.5 hours at 2200° F versus 15 hours at 2760° F for the NS-1, Sec. 3.4.2) resulted in less vanadium and titanium vaporization during sintering. This was further substantiated by sintering weight change and microprobe analysis covered in detail in Section 3.5.1. The resultant higher concentration of these two elements in the silicided coating created a greater driving force for the undesirable



EDGE VIEW

Magnification: 40X



FLAT AREA

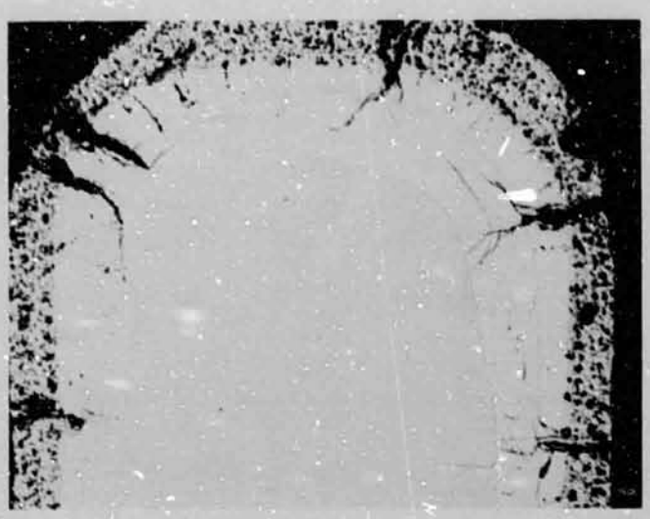
Silicide of Modifier Alloy

Silicide of Diffusion Zone Between Modifier and T222 Alloy

T222 Alloy

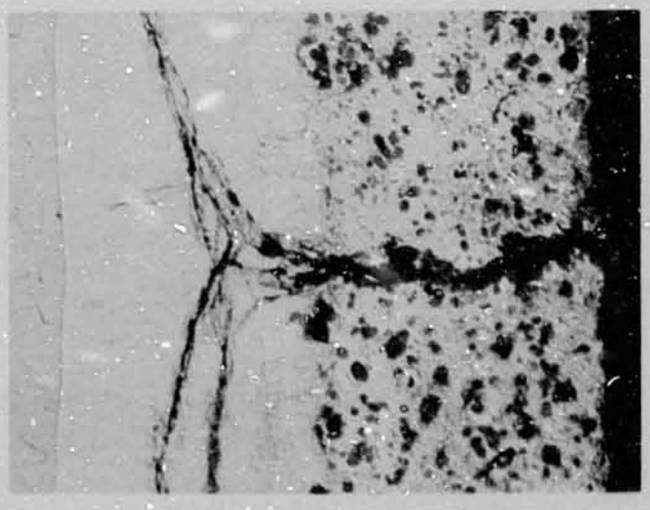
Magnification: 250X

FIGURE 12. NS-12 MODIFIER AFTER SILICIDING



EDGE VIEW

Magnification: 40X



FLAT AREA

Magnification: 200X

FIGURE 13. SILICIDED NS-13 MODIFIER ALLOY

TABLE VII

X-RAY FLUORESCENCE ANALYSIS OF NS-1 AND NS-13
COATED SPECIMENS OXIDIZED AT 2400° F

Modifier Alloy	Oxidation Time (hr)	Counts/Second, Above Background						
		Pd	Mo	W	Ta	V	Ti	Si
NS-13 (35Mo35W14.5Ti14.5V1Pd)	238	16	2574	571	5	67	1193	2078
NS-1 (35Mo35W15Ti15V)	209	Nil	3212	927	Nil	27	374	7109

glass formation. The titanium content of the W-2.5Ti-0.25Ni alloy, investigated in Reference 1, was apparently low enough to yield the observed good oxidation resistance and minimal glass formation.

3.2.3 Series III Modifiers - High W/Mo Ratios

Of the coatings tested to this point in the program, one coating that always rated superior was NS-4 (20Mo50W15Ti15V). To further evaluate this high W/Mo ratio modification of NS-1, four additional chemistries were prepared. These four chemistries are listed in Table VIII.

TABLE VIII

SERIES III MODIFIER COMPOSITIONS WITH HIGH W/Mo RATIO

Designation	Composition (wt %)	Change
NS-14	15Mo65W10Ti10V	Retain high W/Mo ratio, lower Ti + V
NS-15	15Mo65W15Ti5V	Retain high W/Mo ratio, lower V content
NS-17	28Mo45W15Ti15V	Retain NS-4 Ti/V ratio and concentration, lower W/Mo ratio
NS-18	20Mo50W20Ti10V	Retain NS-4 W/Mo ratio and concentration, raise Ti/V ratio

The slurries were prepared in the standard manner using 5-micron W and Mo powders milled together with vanadium and titanium hydride. The coatings were applied and sintered for 15 hours at 2760° F to produce 0.004- to 0.005-inch thick

modifiers (55 to 75 mg/cm^2). The specimens were subsequently silicided for 15 hours at 2150° F to produce a deposit of 40 to 50 mg/cm^2 of silicon with a coating thickness increase of 0.004 inch. These coatings all performed well in cyclic oxidation, bend tests, and ballistic impact. The coating NS-15, which had 50 percent porosity in the as-sintered condition, retained 10 percent porosity as a silicide (shown metallographically in Fig. 14). This coating had good coating-substrate bonding combined with low interconnected porosity. Both of these factors are considered to be desirable and the coating (NS-15) was shown to be superior to any other previously tested in ballistic impact at 1600° F followed by 1600° F oxidation.

3.2.4 Series IV Glass Former and Glass Modifier Additions

The previous evaluations with NS-3Fe, -10Fe and -16 have shown the beneficial effects of iron additions with respect to producing good coating-substrate bonding and higher density modifier deposits.

To evaluate the influence of a low-temperature glass former, boron, and the glass modifier iron, additions of these elements were made to three modifier chemistries as shown in Table IX. The basic chemistries were selected because they had

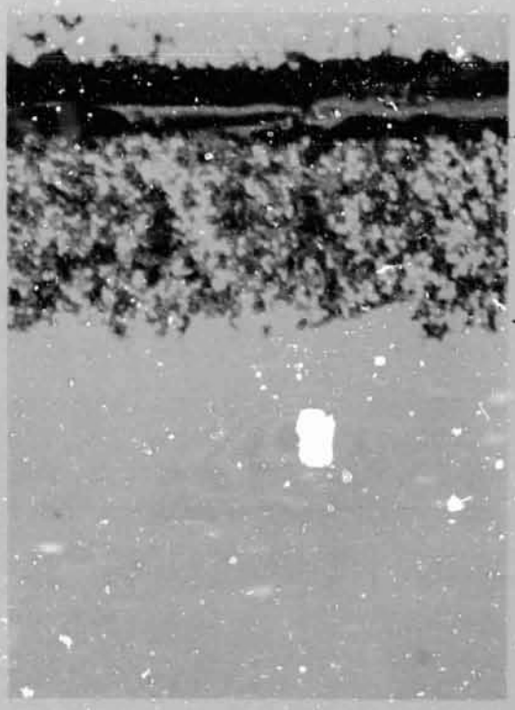
TABLE IX

SERIES IV MODIFIER COMPOSITIONS WITH GLASS FORMERS

Number	Modifier	Change
NS-19	41.5Mo41.5W15V2Fe	Add Fe to NS-9
NS-20	42Mo42.5W15V.5B	Add B to NS-9
NS-21	68Mo20W5Ti5V2Fe	Add Fe to NS-10
NS-22	69.5Mo20W5Ti5V.5B	Add B to NS-10
NS-23	15Mo63W15Ti5V2Fe	Add Fe to NS-15
NS-24	15Mo64.5W15Ti5V.5B	Add B to NS-15

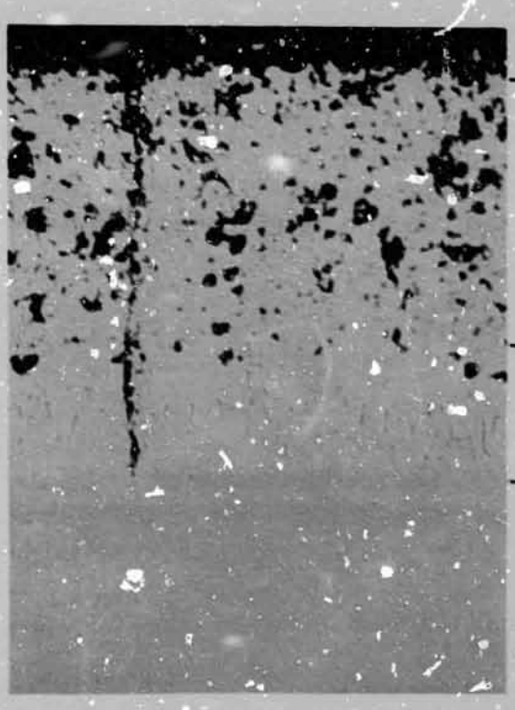
been thoroughly evaluated in the program and represented extremes in the concentrations of Mo, W, and V. The high vanadium coating (NS-9) was included primarily to determine if the 1600° F impact and subsequent oxidation resistance could be improved by Fe or B additions.

The coatings were prepared by milling W, Mo, vanadium and titanium hydride powders together with the Fe or B addition in the E-4 vehicle. The coating was applied by spray techniques and sintered 15 hours at 2760° F. The resultant deposits (65 to 75 mg/cm^2 0.004 to 0.006 inch) were silicided as described in Section 3.1.2 to produce



Modifier

Magnification: 250X



Silicided Modifier

Silicided Substrate

Magnification: 250X

FIGURE 14. NS-15 MODIFIER AS SINTERED AND AS SILICIDED

coating weight gain and thicknesses of 40 to 50 mg/cm^2 (0.004 inch).

Cyclic oxidation and bend testing and impact followed by oxidation testing showed NS-23 (NS-15 plus 2 percent Fe) to be superior to any coating previously tested. The addition of iron produced coatings with low pore volume in the as-silicided condition.

The coatings with boron additions developed silicides with high pore volumes (>15 percent) and consequently short 1600° F oxidation lives.

The microstructure of NS-23, shown in Figure 15, shows more alloying than was noted for the iron-free equivalent (Fig. 14). The improvement in impact performance is attributed to a possible increase in titanium retention by the substrate due to liquid-phase sintering and increased coating-substrate bonding. The effects of iron were proven to be the result of alloying and sintering, since microprobe analysis indicated no detectable iron residue in the NS-23 coating after siliciding.

3.2.5 Series V - Selected Coating for Evaluation on FS-85

A group of five of the coatings, which had exhibited outstanding performance on T222, were further tested for protection of the columbium-base alloy FS-85. The coatings selected for evaluation were NS-1, -3, -4, -15, and -23. The NS-1 (formerly TNV-7) served as a standard for all comparisons throughout the program. The NS-3 had performed well in all evaluations except torch testing. The coatings NS-4, -15 and -23 had all exhibited superior performance in all tests. The only measurable variation had been in 1600° F impact testing followed by oxidation, discussed in Section 3.3.4.

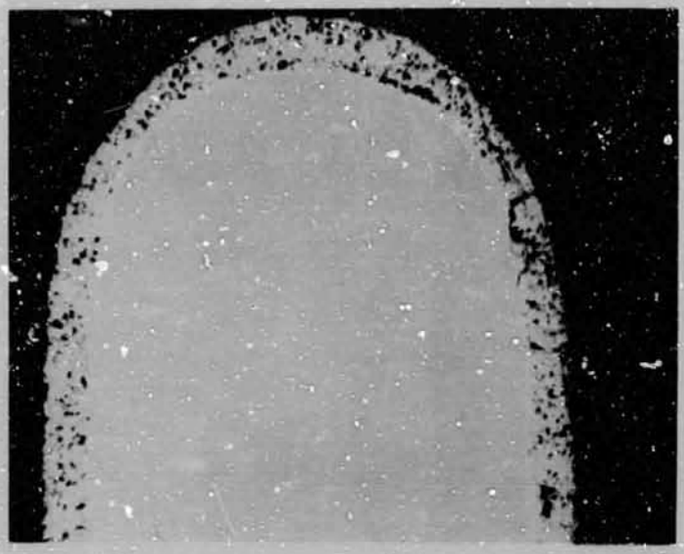
The microstructures, Figures 16, 17, and 18, show the coatings NS-1, -4, and -23 on FS-85 in the as-silicided condition. The microstructures of both NS-1 and -4 are very similar to that observed for the coatings on T222; the only significant difference being the absence of a visible titanium-rich diffusion zone at the silicide-substrate interface. The NS-23 coating had an excessively thick silicide layer between the substrate and the silicided modifier which could contribute to coating spall and failure.

3.3 INITIAL SCREENING OF ALL COMPOSITIONS

3.3.1 Screening Test Techniques

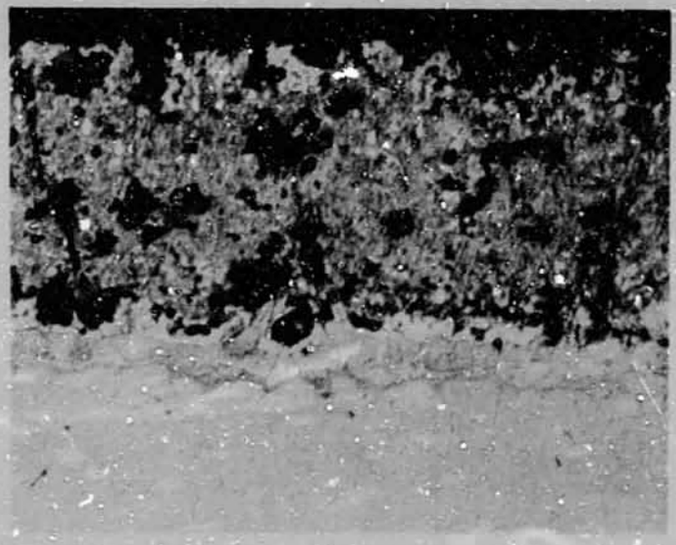
Furnace Oxidation

Furnace oxidation testing of the silicide coated specimens was conducted in static air in electrically heated furnaces maintained at either 1600 or 2400° F for



EDGE VIEW

Magnification: 40X

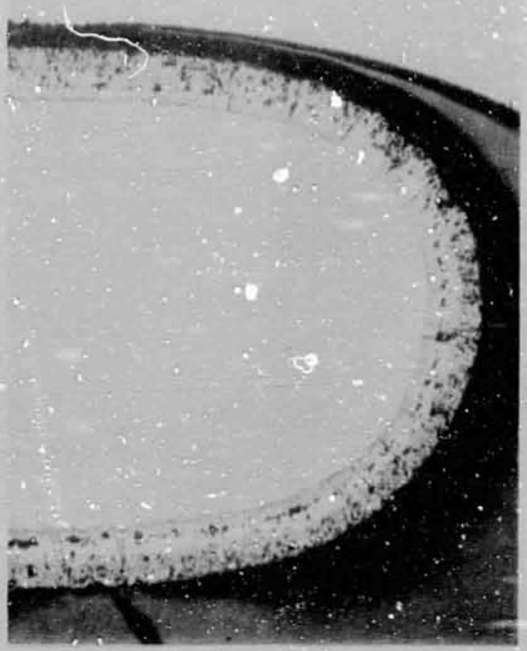


FLAT AREA

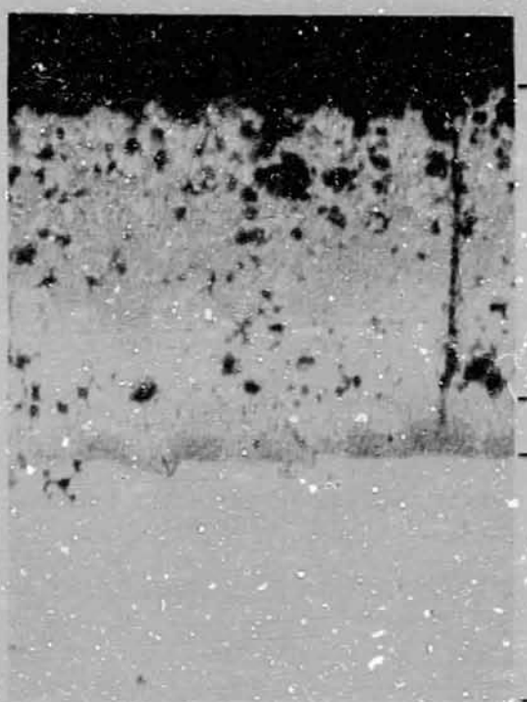
Magnification: 250X

FIGURE 15. NS-23 MODIFIER AFTER SILICIDING

EDGE VIEW



Magnification: 40X



FLAT AREA

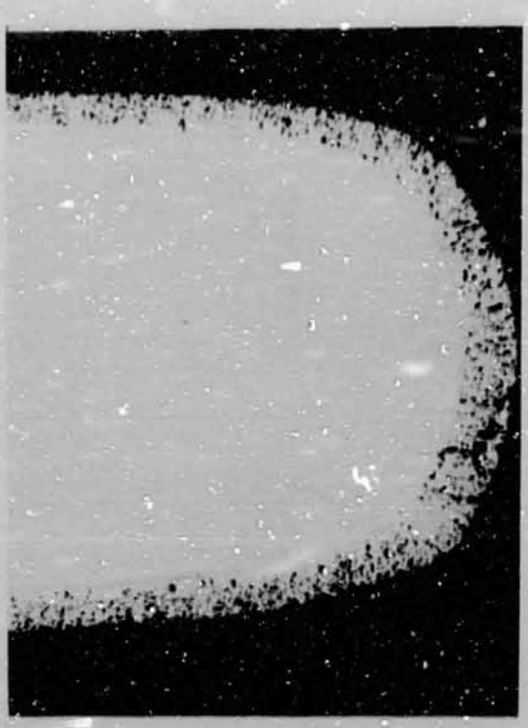
Silicide of Modifier Alloy

Silicide of Substrate

Substrate

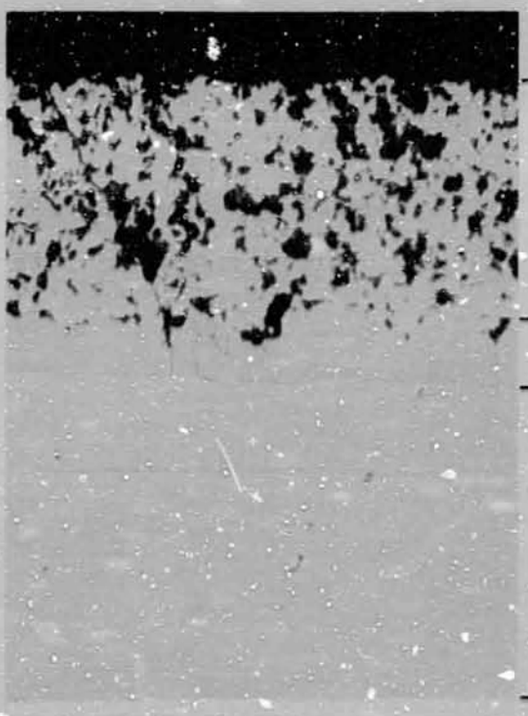
Magnification: 250X

FIGURE 16. NS-1 MODIFIER AFTER SILICIDING ON FS-85 SUBSTRATE



EDGE VIEW

Magnification: 40X



FLAT AREA

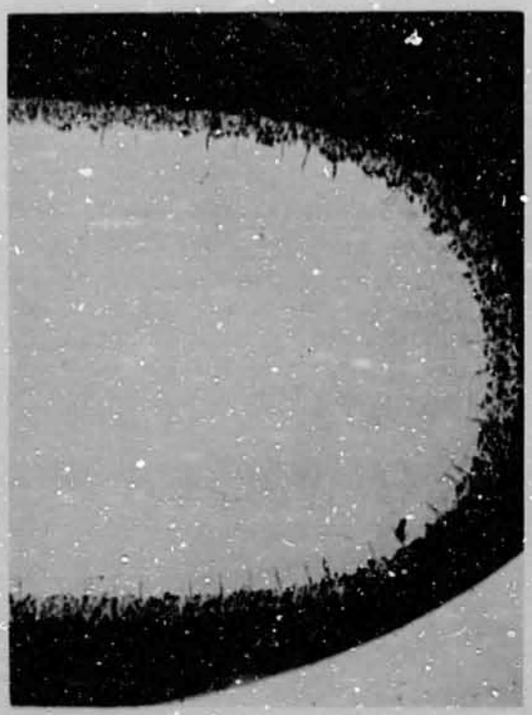
Silicide of Modifier Alloy

Silicide of Substrate

Substrate

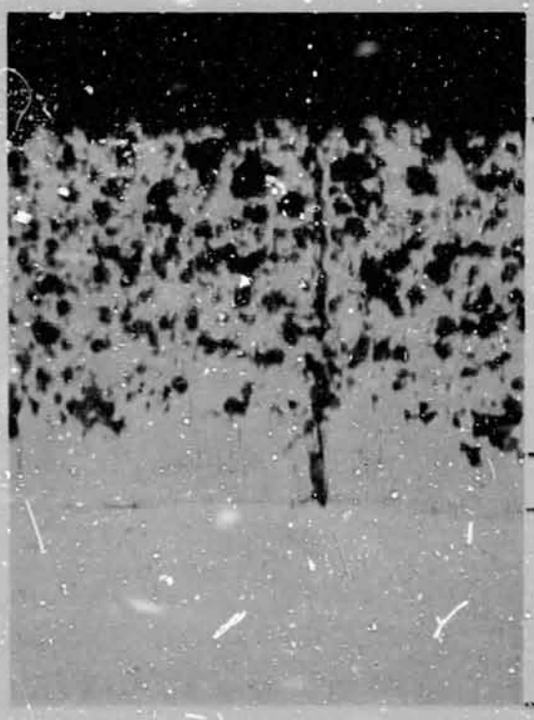
Magnification: 250X

FIGURE 17. NS-4 MODIFIER AFTER SILICIDING ON FS-85 SUBSTRATE



EDGE VIEW

Magnification: 40X



FLAT AREA

Silicide of Modifier Alloy

Silicide of Substrate

Substrate

Magnification: 250X

FIGURE 18. NS-23 MODIFIER AFTER SILICIDING ON FS-85 SUBSTRATE

200 hours. The specimens were supported on lengths of triangularly shaped Dyna-Quartz. (Dyna-Quartz is a felt of quartz fibers produced by the Johns Manville Company.) The Dyna-Quartz rested on fire brick to provide free access of all sample surfaces to the atmosphere. The specimens were oxidized for two 2-hour cycles and one 16-hour cycle each week day and for a 65-hour cycle over the weekend. The samples were weighed after each of the first three oxidation cycles and at the end of the test.

Bend Testing

The three-point loading type bend test fixture shown in Figure 19 was used in appraising the ductility of the specimens in the as-coated and as-oxidized conditions. As noted in Figure 19, the radius of the upper ram was 0.078 ± 0.003 inch and was used in conjunction with a ram speed of 0.5 inch/minute. The use of this particular ram resulted in a 1T radius bend test, which is more severe than the normal 4T radius bend test recommended in MAB-201M. The 1T radius was used because it was considered more sensitive for comparing the relative ability of the different coatings to maintain the ductility of the substrate. The test fixture was used in conjunction with an Instron test machine provided with a 1000-pound full scale load cell. Each test yielded a plot of ram load versus ram travel, which was subsequently converted to bend angle by reference to a calibration curve. The travel at which a visible crack could be seen in the substrate and the travel corresponding to the failure of the substrate were noted. The failure point was arbitrarily taken as the point at which the ram load had dropped to 10 percent of the maximum ram load sustained by the substrate.

Ballistic Impact

The ballistic impact apparatus selected for this evaluation, shown in Figure 20, consisted basically of a Crosman .22 caliber air rifle which was charged with nitrogen to a known pressure. The stock of the rifle was removed and the rifle was mounted on the stable aiming fixture shown schematically in Figure 21. The gun was aimed by insertion of a long rod through the aiming hole and into the gun barrel. The gun was loaded with a 3/16-inch chromium steel ball (0.44 gram). The conditions for the test are noted below:

- Room-Temperature Impact

  The specimens were clamped on one end between two aluminum blocks bolted to the back wall of the enclosure shown in Figure 22 and impacted at 170 ± 15 feet per second (condition 1: 100 psig nitrogen chamber pressure). Two specimens of each coating system were furnace oxidized after impact at 1600 and 2400° F for up to five 2-hour cycles. The surviving specimens were impacted a second time in a different location at 240 ± 40 feet per second (condition 2: 200 psig nitrogen chamber pressure).

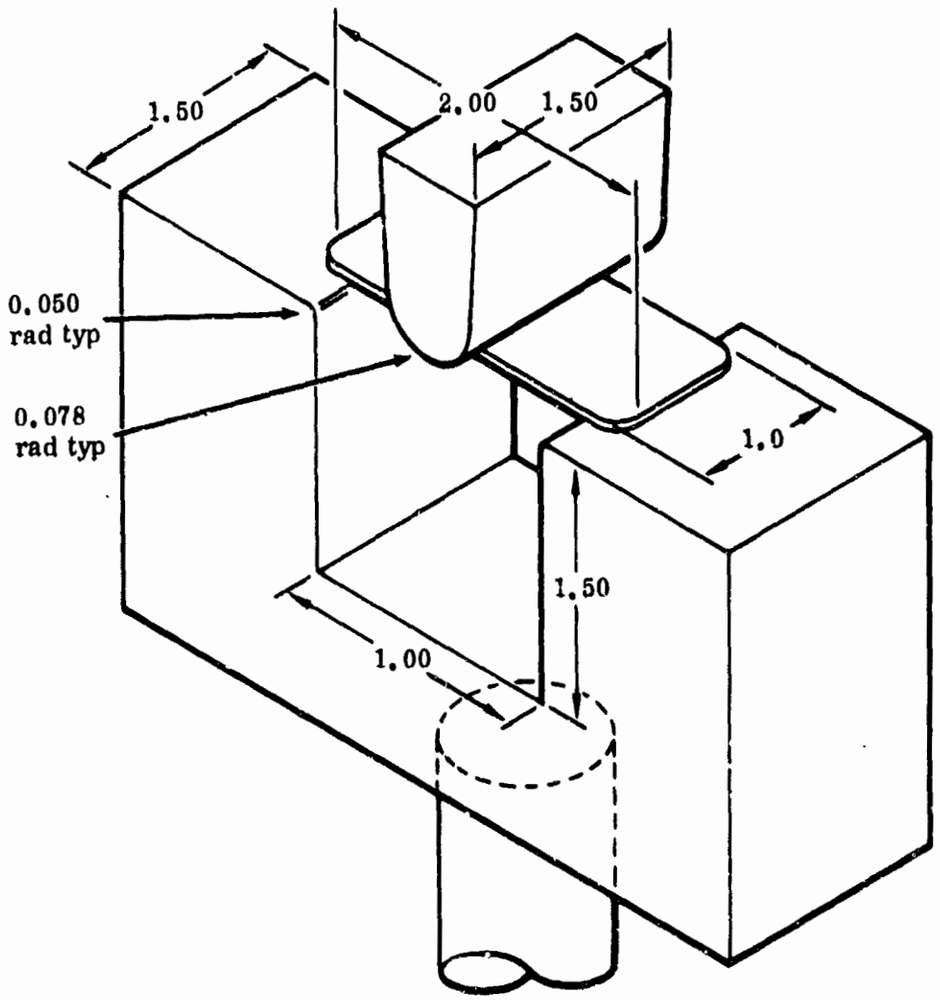


FIGURE 19. BEND TEST FIXTURE

Furnace oxidation testing at each temperature followed using one 1-hour and two 2-hour cycles for T222 substrate and one 1-hour, two 2-hour, and one 5-hour cycle for each coated FS-85 substrate.

- 1600° F Impact

Two specimens of each coating system were impacted at 1600° F ± 5° F under impact condition 1 while being held loosely by both ends in the Inconel 600 fixture shown in Figure 23. Furnace oxidation followed at 1600° F for the same time intervals used for condition 2 room-temperature impacts. Surviving specimens were impacted (condition 2) in a

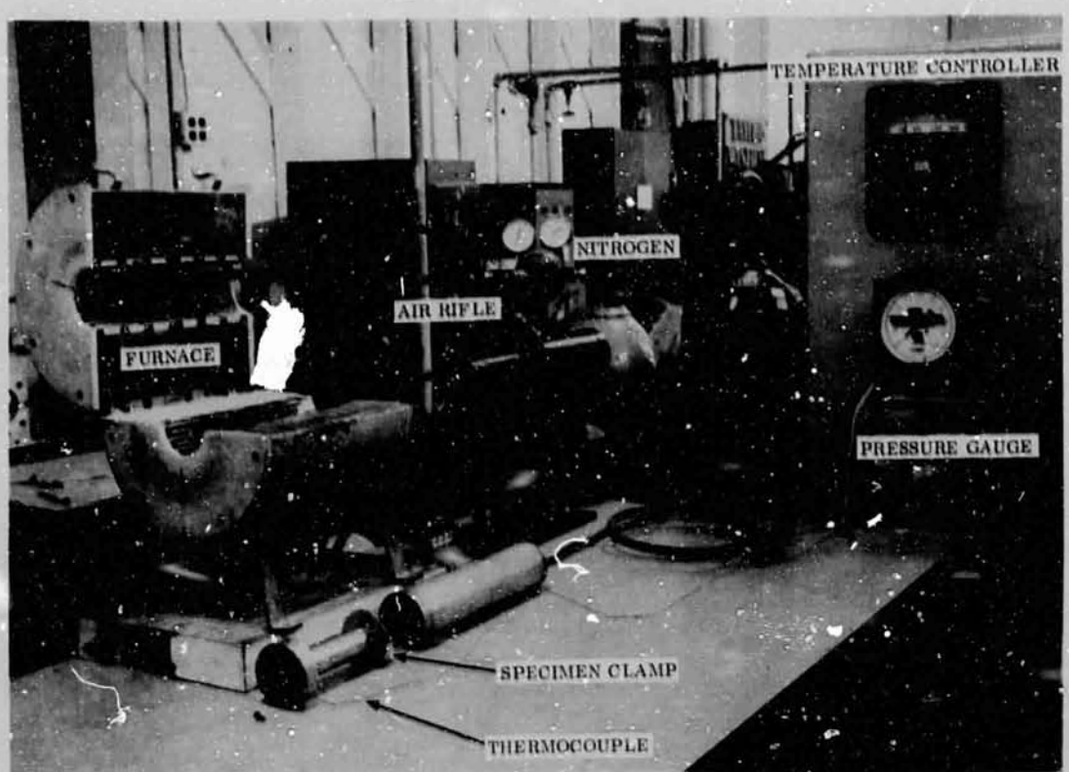


FIGURE 20. BALLISTIC IMPACT APPARATUS

different location and returned to test for the same sequence of 1600° F oxidation. The elevated temperature impacting was conducted with the specimen inside a clam shell furnace.

- Metallographic Examination

Numerous techniques have been evaluated for the metallographic examination of the impacted specimens to obtain views of the desired location on the specimens. Samples were cut leaving a specified distance from the edge of the specimens to the center of impact. The specimens were subsequently mounted and polished, attempting to grind back the desired distance to reach the impact center. Samples were also mounted together with a marker of a thickness comparable to the amount to be ground away to reach the center of the impact. Both of these techniques produced results less than satisfactory.

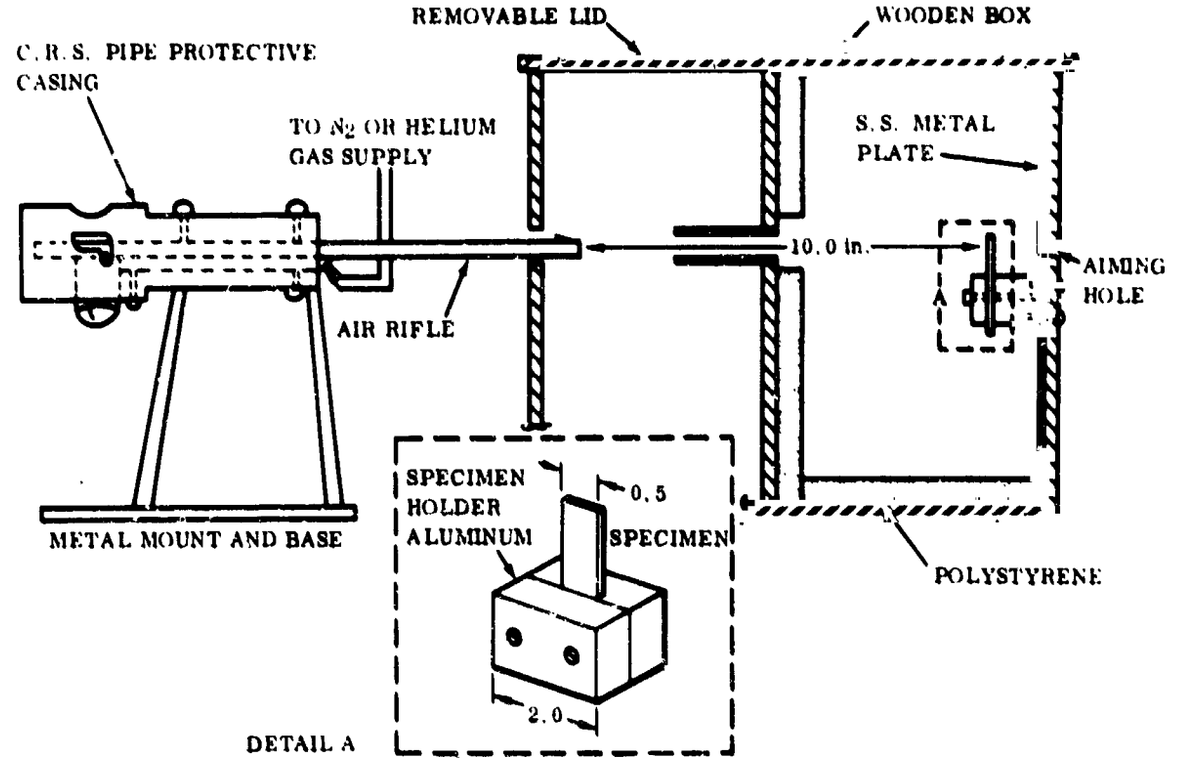


FIGURE 21. DESIGN OF PROTECTIVE HOUSING FOR AIR RIFLE

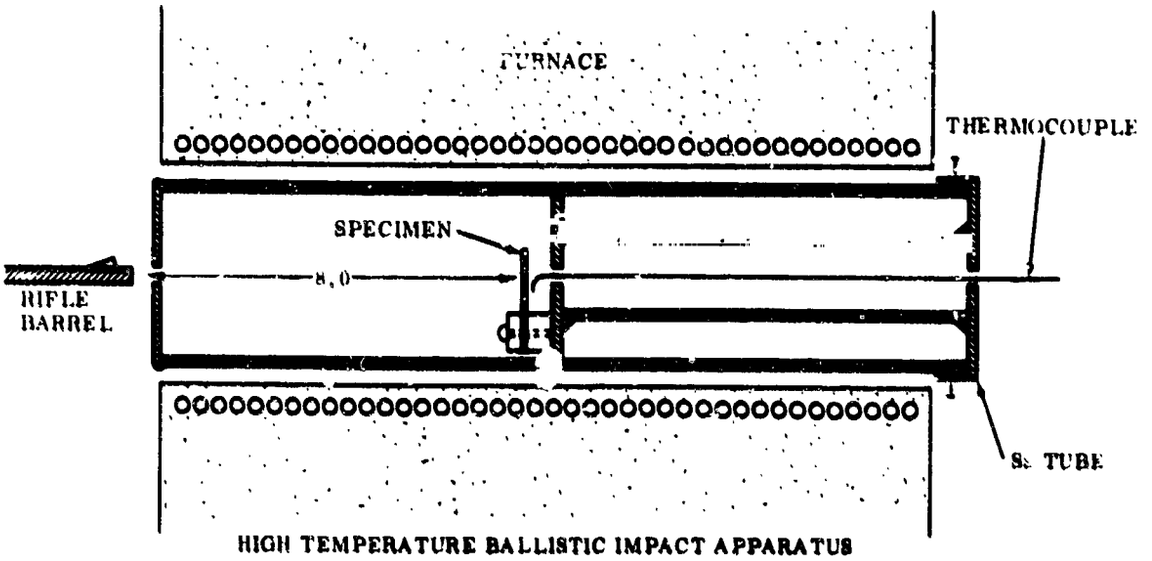


FIGURE 22. DESIGN OF SPECIMEN VISE AND FURNACE INSERT

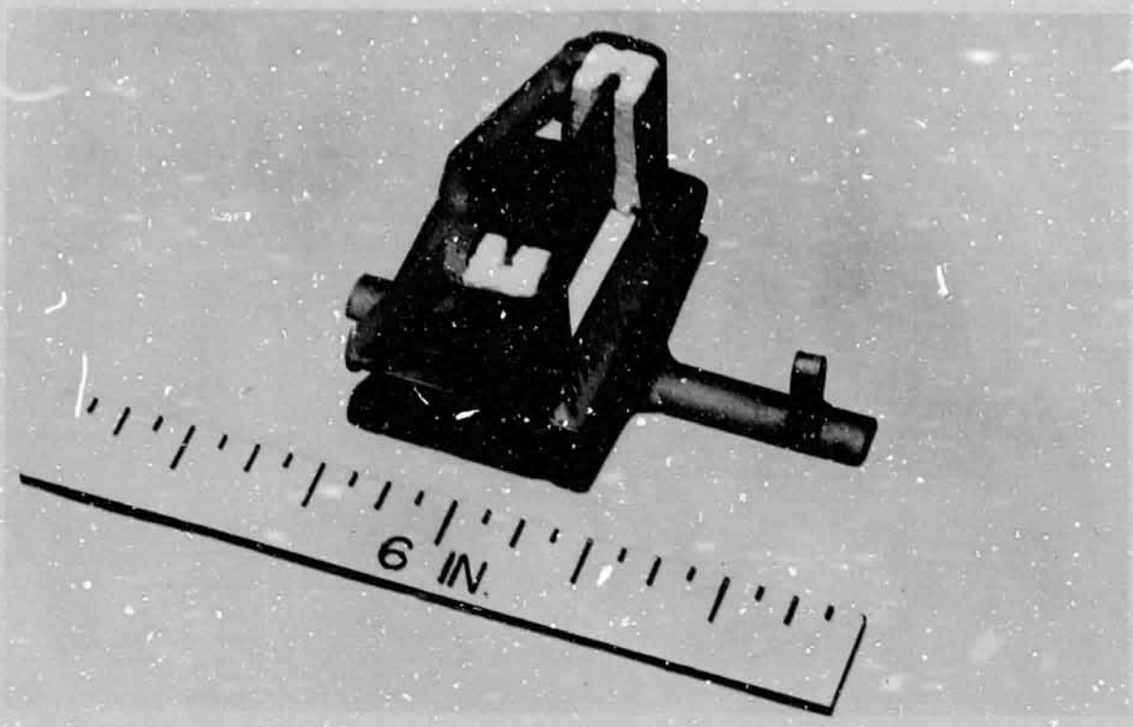


FIGURE 23. INCONEL 600 FIXTURE FOR BALLISTICALLY IMPACTING SPECIMENS AT 1600° F (with specimen in place)

The technique that has proven both satisfactory metallographically and convenient mechanically utilizes clear epoxy resin as the mounting agent. This process permits the metallographer to visually observe the impacted zone during the grinding process so that the desired point required for metallography may be reached precisely.

Samples were mounted in the clear epoxy resin (Marglas Type A655 Resin/555 Hardener) and cured 16 hours at 170° F. The epoxy was blended from 100 parts by weight resin to 7 parts of hardener.

Torch Testing

The unit used for torch testing is shown in Figure 24 and was used on NS-1 to NS-10 modifiers only.

One 0.062-inch by 1-inch by 2-inch coated specimen was held up by layers of Micro-Quartz felt (Johns Manville Corp.) between bricks resting on the turntable of the torch testing apparatus. The specimens were heated by two size 10, Victor type

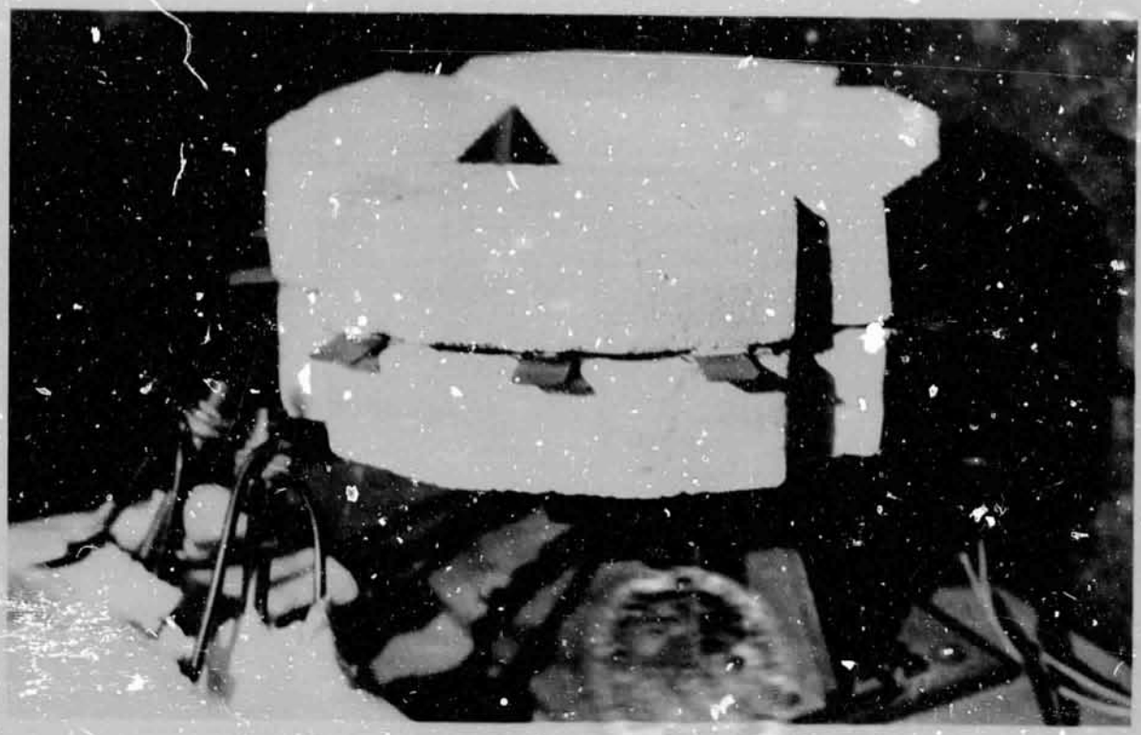


FIGURE 24. PROPANE-OXYGEN TORCH TEST SETUP

12, multiflame torches operating on propane and oxygen. Figure 24 reveals that the torches were modified by soldering a water cooling coil around each nozzle tip and that the flames impinged on the lower flat face of the specimens.

The turntable operated at 0.25 rpm so that the sample was in a hot zone approximately 7 percent of the total 10-hour test period. No temperature difference was observed between different composition coatings when the temperature was measured with an optical pyrometer. Tests were performed at corrected temperatures of 2530, 2640, and 2685° F; a value of 0.7 was used for the emittance at 0.65 microns (Ref. 5).

3.3.2 Furnace Oxidation Test Results

The cyclic furnace oxidation testing of the first ten coatings was conducted as described in Section 3.3.1. Examination of the data in Table X reveals a large number of coatings exceeded the 200-hour milestone without problems. (The tests were nominally for 200 hours but, due to over-the-weekend testing, some specimens were exposed for nearly 240 hours.) Tested coupons for each chemistry are shown in Figure 25. Of the first ten compositions, NS-7 (45Mo-45W5Ti5V modifier alloy) displayed the highest failure frequency and also the highest average weight gain. It must

TABLE X

COATING APPLICATION AND FURNACE OXIDATION TEST RESULTS - COATINGS(A) ON T222

Modifier Alloy	Run No. R-( )	Sintered Wt. Gain ($mg\ cm^2$) and Thickness (10^{-3} in.)	Siliciding Wt. Gain ($mg\ cm^2$) and Thickness (10^{-3} in.)	Silicon Modifier Atomic Ratio	Oxidation Lives			
					Hours at 1600 F	Avg. Wt. Gain ($mg\ cm^2$)	Hours at 2400 F	Avg. Wt. Gain ($mg\ cm^2$)
NS-1 35Mo35W15Ti15V	27(B)	60 4.5	44 3.2	2.2	3 at >209	1.4	3 at >209	3.5
NS-2 35Mo35W10Ti20V	30(B)	62 4.6	47 4.0	2.3	3 at >214	1.7	3 at >214	3.0
NS-3 35Mo35W20Ti10V	31(B)	54 4.0	40 3.7	2.3	3 at >214	1.4	3 at >214	2.9
NS-4 20Mo50W15Ti15V	16	60 4.4	37 3.2	2.0	3 at >218	1.1	3 at >218	3.0
NS-5 50Mo20W15Ti15V	[illegible]	56 4.4	42 3.6	2.2	3 at >218	0.9	3 at >213	3.5
NS-6 40Mo40W10Ti10V	40(B)	57 4.5	41 3.8	2.7	3 at >209	2.5	3 at >209	3.3
NS-7 45Mo45W5Ti5V	28	69 5.7	48 3.9	2.3	2, 3, 214	2.9	2, 2 at >214	3.6
NS-8 40Mo40W5Ti15V	19	72 5.4	50 4.0	2.4	129, 2 at >218	1.8	3 at >218	3.4
NS-9 42.5Mo42.5W15V	21	79 5.7	53 4.6	2.5	3 at >218	1.8	3 at >218	3.4
NS-10 70Mo20W5Ti5V	29	73 5.3	47 4.0	1.9	3, 2 at >214	2.1	3 at >214	3.2

(A) Vanadium having approximately 0.5% oxygen used.
(B) Titanium added as TiH_2.

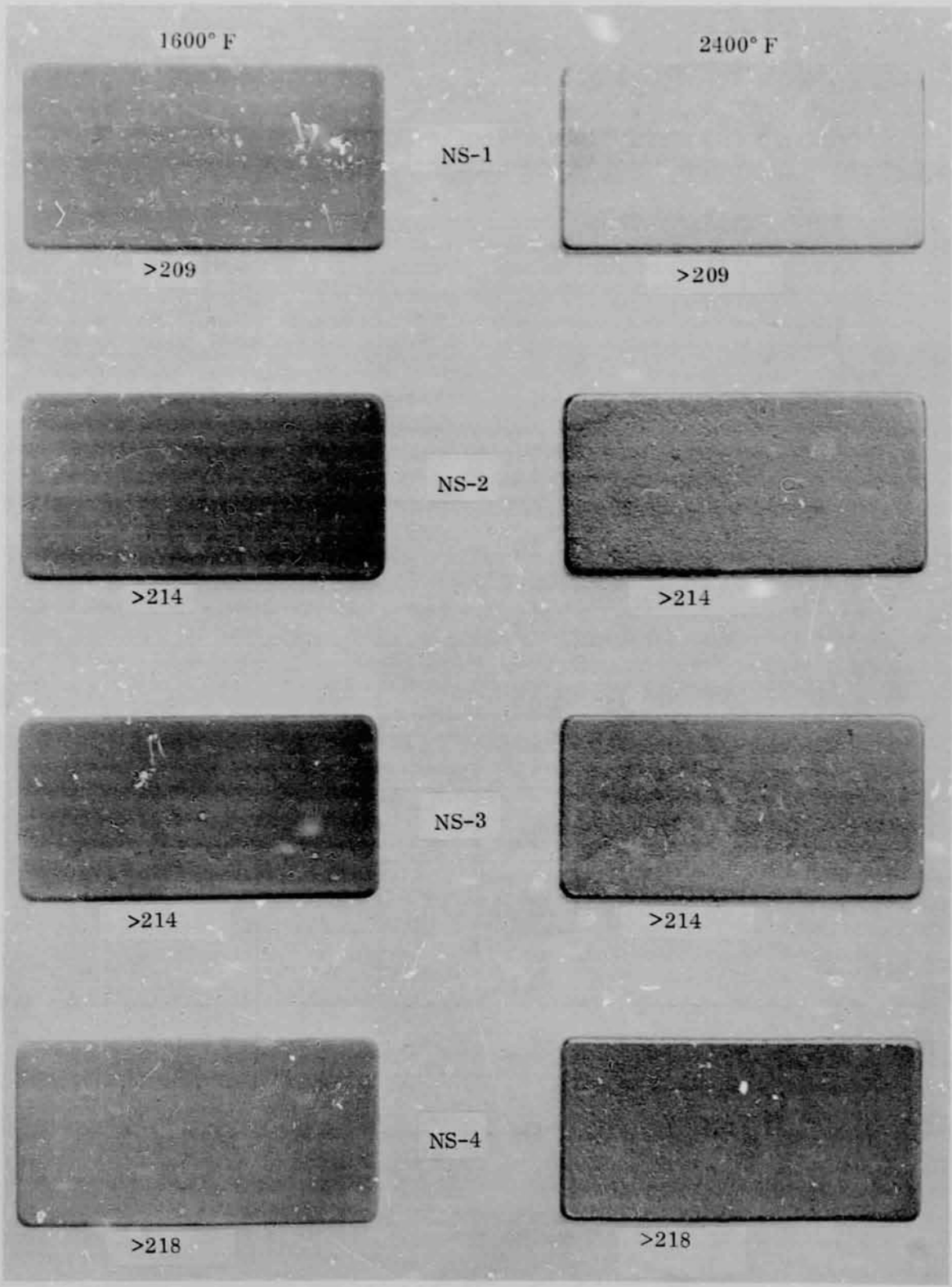


FIGURE 25. COATED T222 TEST SPECIMENS AFTER CYCLIC OXIDATION TESTING AT 1600° F AND 2400° F (Sheet 1 of 6)

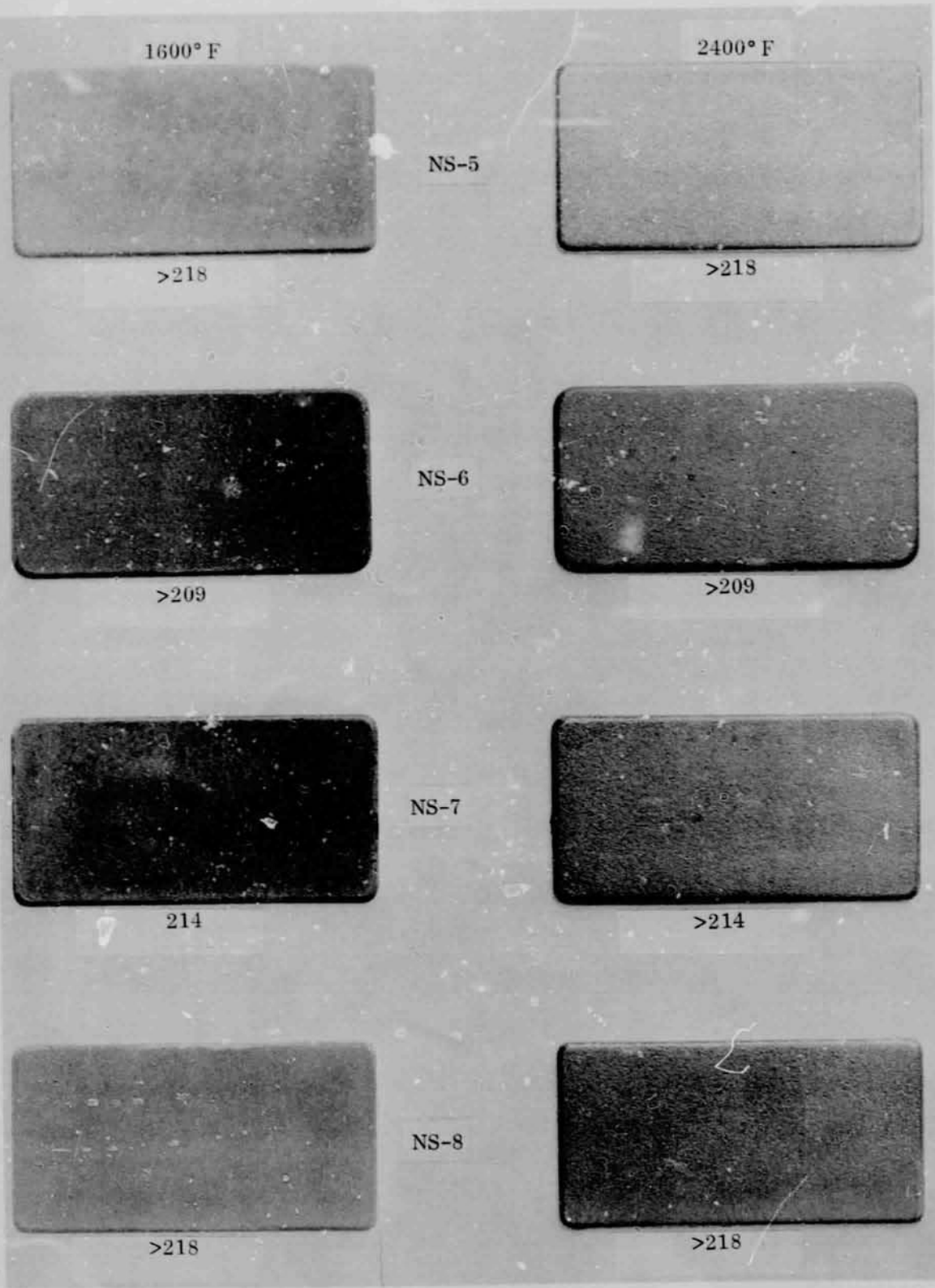


FIGURE 25. COATED T222 TEST SPECIMENS AFTER CYCLIC OXIDATION TESTING AT 1600° F AND 2400° F (Sheet 2 of 6)

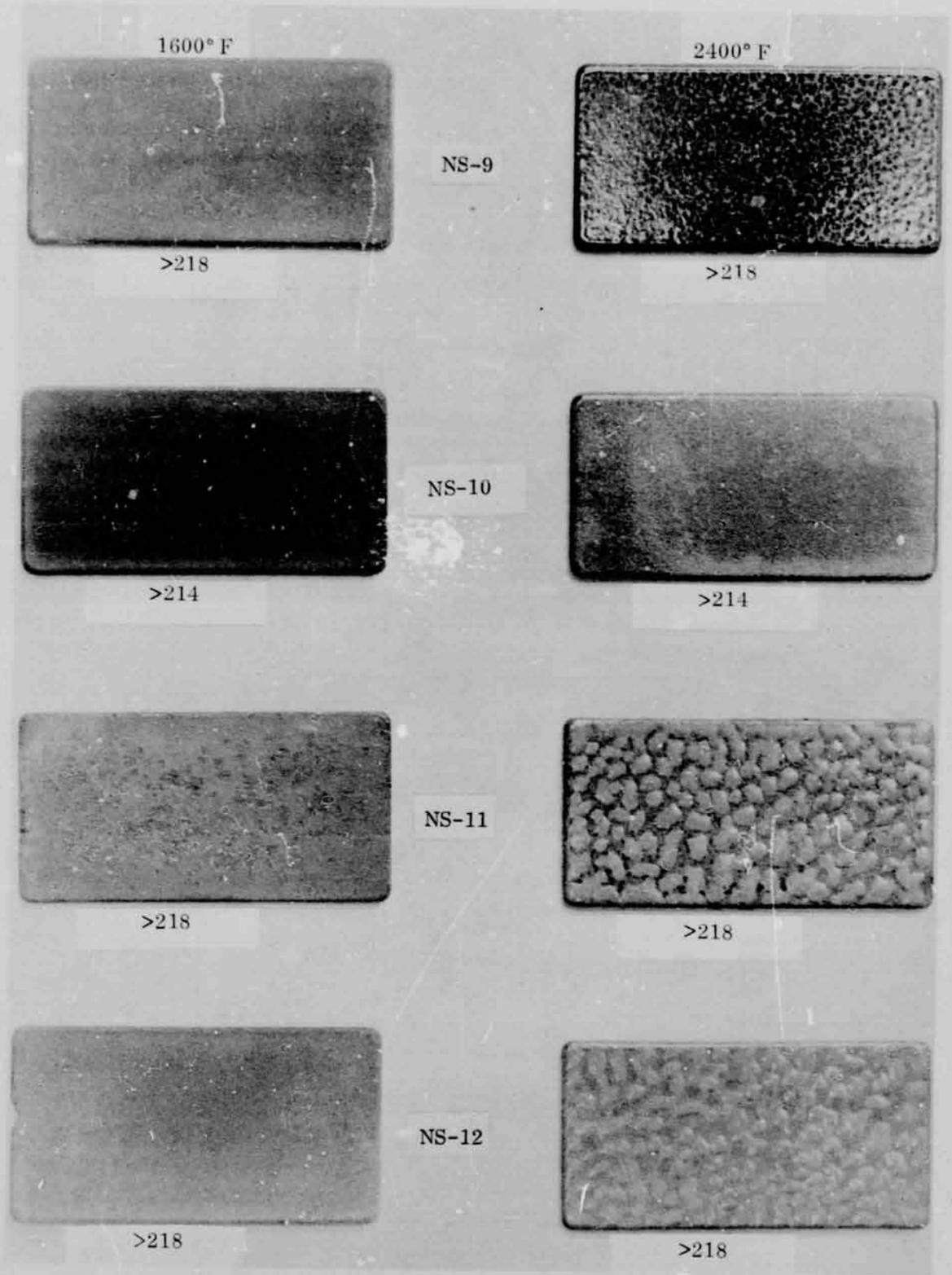


FIGURE 25. COATED T222 TEST SPECIMENS AFTER CYCLIC OXIDATION TESTING AT 1600° F AND 2400° F (Sheet 3 of 6)

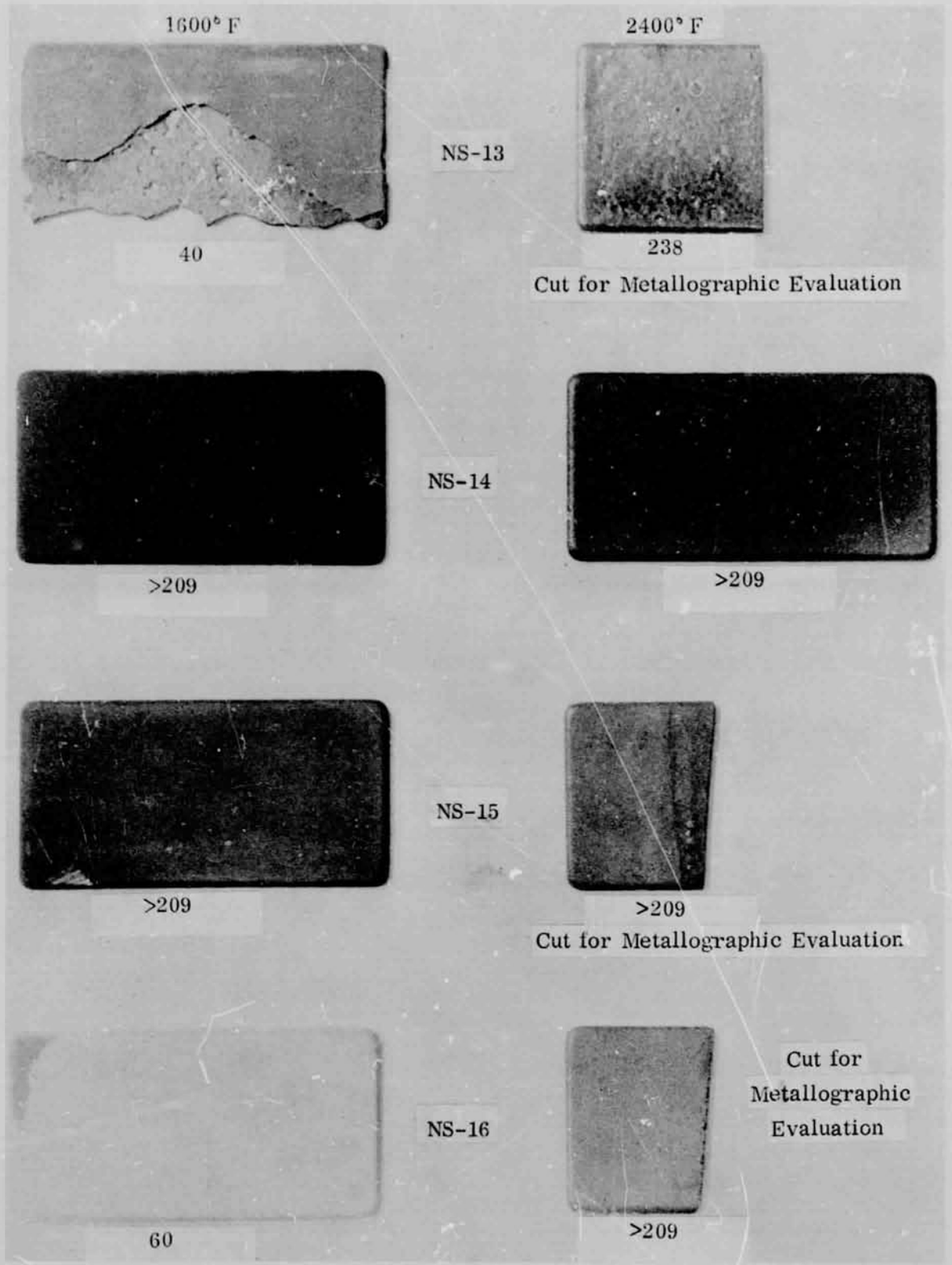


FIGURE 25. COATED T222 TEST SPECIMENS AFTER CYCLIC OXIDATION TESTING AT 1600° F AND 2400° F (Sheet 4 of 6)

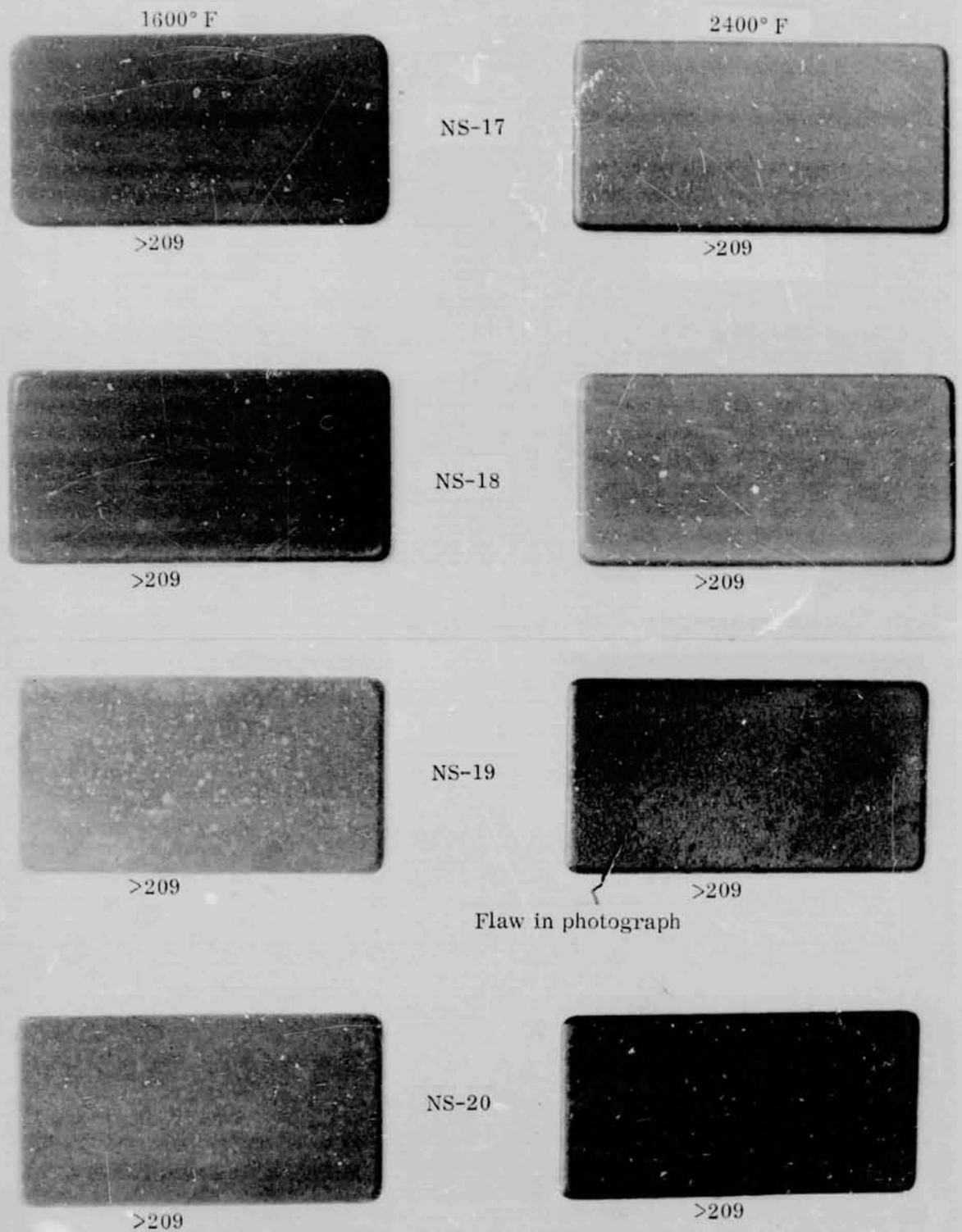


FIGURE 25. COATED T222 TEST SPECIMENS AFTER CYCLIC OXIDATION TESTING AT 1600° F AND 2400° F (Sheet 5 of 6)

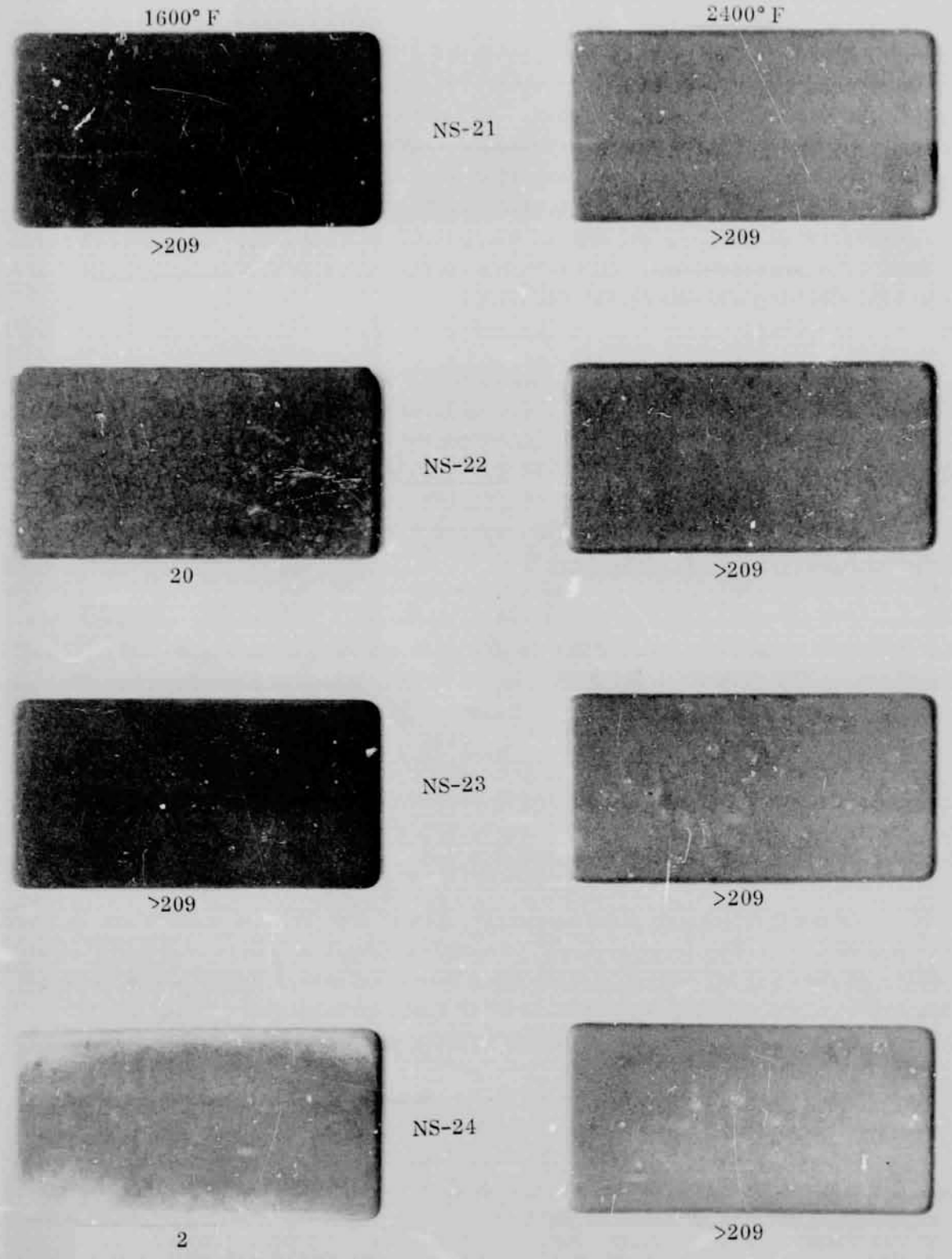


FIGURE 25. COATED T222 TEST SPECIMENS AFTER CYCLIC OXIDATION TESTING AT 1600° F AND 2400° F (Sheet 6 of 6)

be pointed out, however, that the NS-7 modifier alloy was prepared using powdered titanium metal rather than titanium hydride. The initial series of tests on NS-6, prepared with powdered titanium metal, produced coatings which all failed during the first 2-hour cycle of 1600° F furnace oxidation. When titanium hydride was substituted for the elemental powder, the NS-6 experienced no failures at either 1600 or 2400° F when tested for over 200 hours. It is highly probable that the use of titanium hydride in the preparation of NS-7, -8, and -10 would result in a corresponding improvement in their oxidation resistance. This improved performance is apparently the result of improved sintering and subsequent siliciding.

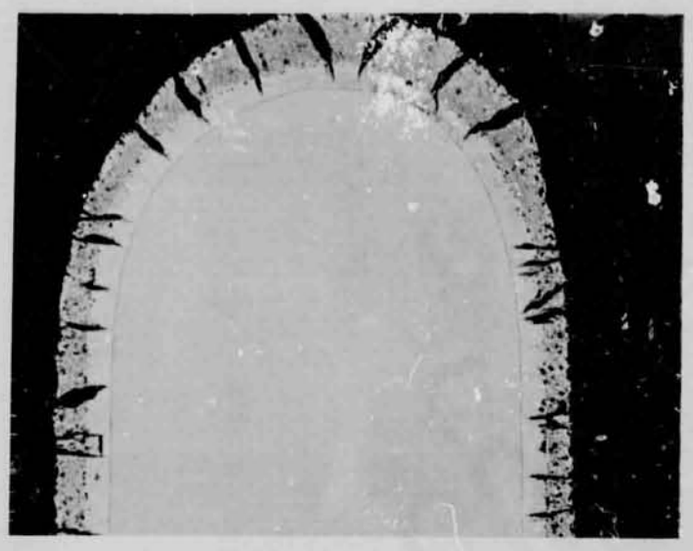
The microstructure of the oxidized coatings were very similar to the TNV-7 coating (Ref. 1). Typical examples of the oxidized structures, NS-4 and -9, are shown in Figures 26 and 27. Changes from the as-coated structure, Figure 2, consist primarily of enlargements of the relatively uniformly spaced craze cracks, a thickness increase of approximately 0.0015 inch in the dense silicide sublayer, the formation of a dense surface oxide layer, and the appearance of a relatively thick (0.005 inch) metallic zone which became apparent in T222 coated with high titanium content coatings such as NS-4 after 200 hours, but was not present with the NS-9 titanium-free coating. The latter observation appears to be the result of titanium diffusion into the substrate. There was no evidence of an increase in substrate oxygen content at the base of any of the craze cracks; thus the coating afforded complete protection throughout the test period.

The furnace oxidation testing of the remaining 16 modifier chemistries (compositions are described in Sec. 3.2.2, 3.2.3 and 3.2.4) was conducted in the same manner as for the first ten coatings. The results are listed in Tables XI through XIV and Figure 25 (Sheets 3, 4, 5 and 6).

Of the two nickel-containing coatings (NS-11 and -12), the one containing 1 percent nickel (NS-12) was more resistant to oxidation (the first failure at either 1600 or 2400° F occurred at 218 hours), but the glass formation (shown in Fig. 25, Sheet 3) on the surface of the specimens oxidized at 2400° F was so excessive as to make both coatings poor candidates for use in a high velocity environment.

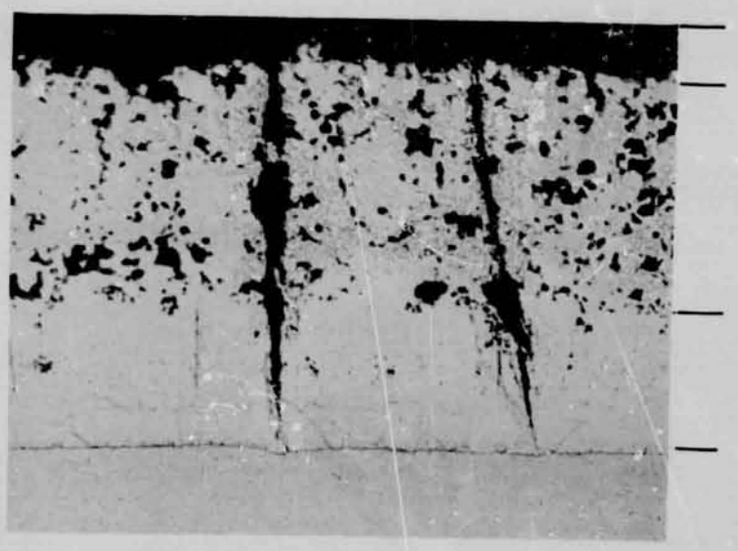
The NS-13, the modification of NS-1 containing 1 percent palladium, was applied in the standard manner except for the reduced sintering time and temperature (1.5 hours at 2200° F). Oxidation of the coated specimens at 1600° F resulted in three failures at 40 hours. In addition, excessive glass formation (visible in Fig. 25, Sheet 4) was observed again in oxidation at 2400° F.

As was previously discussed in Section 3.2.2, an X-ray fluorescent analysis was performed on NS-13. These results, coupled with later investigations of sintering temperature effects (Sec. 3.5.1) reveal a significant difference in vanadium and titanium



EDGE VIEW

Magnification: 40X



FLAT AREA

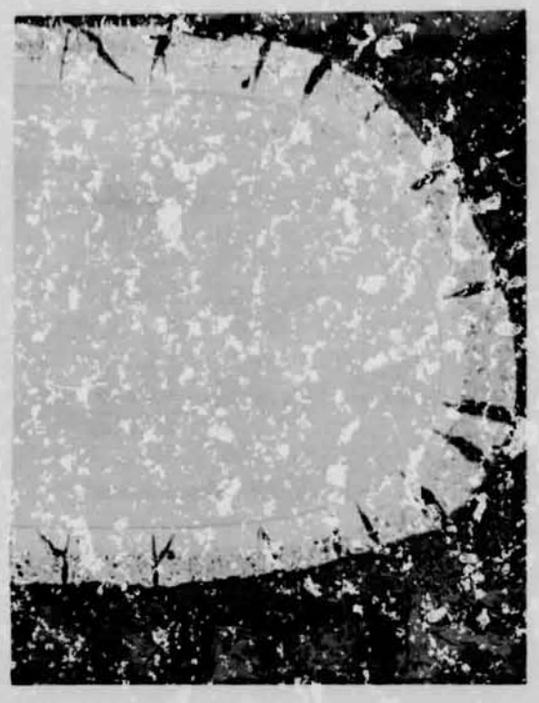
Oxide

Silicide of Modifier

Silicide of T222 Alloy

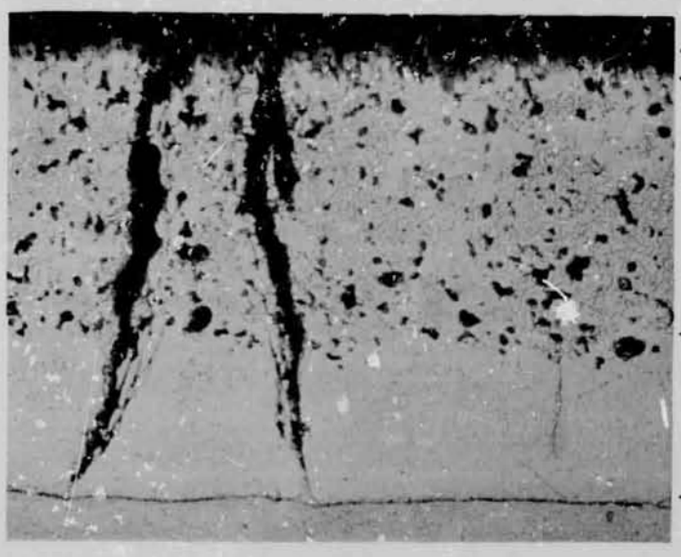
Magnification: 250X

FIGURE 26. NS-4 COATING AFTER OXIDATION TESTING AT 2400° F FOR 218 HOURS



EDGE VIEW

Magnification: 40X



FLAT AREA

Oxide

Silicide of Modifier

Silicide of T222 Alloy

Magnification: 250X

FIGURE 27. NS-9 COATING AFTER OXIDATION TESTING AT 2400°F FOR 218 HOURS

retention with a change of sintering conditions from 1.5 hours at 2200° F to 15 hours at 2760° F. The failure of these sintering aid coatings in oxidation can be largely attributed to the significantly different chemistry from that of the standard NS-1, i.e., the high titanium and vanadium content.

The three chemistries selected to evaluate the substitution of iron for vanadium (NS-3Fe, 10Fe and NS-16) were applied by standard techniques. The results of the cyclic oxidation tests of these three coatings are listed in Table XII and specimens are shown in Figure 25, Sheet 4. The results show increased life, particularly at 1600° F, with increasing Mo/W ratios. Figure 25, Sheet 4 shows a typical NS-16 coated specimen tested at 1600° F, conspicuous by its white appearance. This change in oxide is associated with crystallization of the usually vitreous oxide and is accompanied by rapid weight gain. While iron contributes beneficially to modifier sintering, it cannot be used to completely substitute for vanadium.

Series III

Four high W/Mo atio modifications (NS-14, -15, -17, and -18) of the basic NS-4 compositions were applied by standard methods and tested by cyclic furnace oxidation. The results of the oxidation tests indicated no measurable variation in performance from that of NS-4, all compositions withstood over 200 hours of exposure at 1600 and 2400° F. The results are listed in Table XIII and specimens are shown in Figure 25, Sheets 4 and 5.

Series IV

The application of this series of coatings that add B or Fe in addition to W, Mo, Ti and V (Table XIV) was performed using the standard techniques and the 2760° F sintering temperature. The silicon deposition can be considered normal for the modifier.

Oxidation results from the furnace cyclic oxidation tests at 1600 and 2400° F are given in Table XIV. Tested specimens are shown in Figure 25, Sheets 5 and 6. The addition of boron appeared to be deleterious to oxidation resistance at 1600° F with two of the three coatings (NS-22 and -24) failing before 20 hours. The high vanadium content coating, NS-20, showed less adverse effect of the boron addition than NS-22 and -24 and all specimens withstood 200 plus hours at 1600° F. Neither iron nor boron had a measurable adverse or beneficial effect on the coatings when exposed at 2400° F. Iron-containing coatings all survived 200 plus hours at 1600° F; therefore oxidation testing alone was insufficient to establish whether the addition was beneficial or detrimental.

TABLE XI

APPLICATION AND FURNACE OXIDATION TEST RESULTS FOR COATINGS CONTAINING Ni OR Pd AS SINTERING AIDS (ON T222 ALLOY SUBSTRATES)

Modifier Alloy (A) (B) (C)	Run Number	Sintered Weight Gain (mg/cm^2) and Thickness (10^{-3} Inch)	Silicided Weight Gain (mg/cm^2) and Thickness (10^{-3} Inch)	Silicon Modifier Atomic Ratio	Oxidation Results			
					1600°F		2400°F	
					Life (hrs)	Average Weight Gain (mg/cm^2)	Life (hrs)	Average Weight Gain (mg/cm^2)
NS-11 33Mo33W14.2Ti 14.2V5.6Ni	8	62.1/5.6	65.5/6.6	3.2	20, 2 @ > 218	3.0	24, 2 @ > 218	8.0
NS-12 35Mo35W14.5Ti 14.5V1Ni	9	62.2/5.4	62.8/5.6	3.1	2 @ 218 1 > 218	2.0	3 > 218	7.3
NS-13 35Mo35W14.5Ti 14.5V1Pd	26	67.8/5.6	72.2/7.2	3.3	3 @ 40	-	2 @ 238 1 > 238	8.0

(A) Vanadium having approximately 0.5% oxygen added as hydride.
(B) Titanium added as TiH_2.
(C) Modifier sintered 1.5 hours at 2200°F.

TABLE XII

COATING APPLICATION AND FURNACE OXIDATION TEST RESULTS FOR THE EVALUATION OF IRON AS VANADIUM SUBSTITUTE (ON T222 ALLOY)

Modifier Alloy (A)	Run Number	Sintered Weight Gain (mg/cm^2) and Thickness (10^{-3} Inch)	Silicided Weight Gain (mg/cm^2) and Thickness (10^{-3} Inch)	Silicon Modifier Atomic Ratio	Oxidation Results			
					1600°F		2400°F	
					Life (hrs)	Average Weight Gain (mg/cm^2)	Life (hrs)	Average Weight Gain (mg/cm^2)
NS-16 15Mo65W 15Ti5Fe	54	74.4/3.3	50.3/5.9	2.6	3 @ 60	-	189, 2 @ 209	3.5
NS-3Fe 35Mo35W20Ti 10Fe	38	54.1/3.1	44.2/6.0	2.6	2 @ 80	-	149, 169, > 209	3.9
NS-10Fe 70Mo20W5Ti 5Fe	39	67.5/5.2	51.0/4.7	2.1	3 > 209	1.4	3 > 209	4.1

(A) Titanium added as hydride.

TABLE XIII

COATING APPLICATION AND FURNACE OXIDATION TEST RESULTS FOR THE EVALUATION OF NS-4 MODIFICATIONS (ON T222)

Modifier Alloy (A) (B)	Run Number	Sintered Weight Gain (mg/cm^2) and Thickness (10^{-3} Inch)	Silicided Weight Gain (mg/cm^2) and Thickness (10^{-3} Inch)	Silicon Modifier Atomic Ratio	Oxidation Results			
					1600°F		2400°F	
					Life (hrs)	Average Weight Gain (mg/cm^2)	Life (hrs)	Average Weight Gain (mg/cm^2)
NS-14 15Mo65W 10Ti10V	52	73.1/5.1	48.3/4.1	2.6	3 > 209	2.2	3 > 209	3.3
NS-15 15Mo65W 15Ti5V	53	72.5/4.3	41.6/3.6	2.2	3 > 209	1.3	60(C) 2 > 209	3.4
NS-17 28Mo42W 15Ti15V	55	54.0/4.5	40.6/3.6	2.4	189. 2 > 209	5.5	3 > 209	2.9
NS-18 20Mo50W 20Ti10V	56	57.7/4.0	38.1/3.4	2.1	3 > 209	1.7	3 > 209	2.8

(A) Vanadium having approximately 0.5% oxygen added as hydride.
(B) Titanium added as hydride.
(C) Specimen lost in furnace during oxidation test.

TABLE XIV

APPLICATION AND FURNACE OXIDATION TEST RESULTS FOR THE EVALUATION OF COATINGS CONTAINING Fe OR B PLUS W-Mo-Ti-V ON T222

Modifier Alloy (A) (B)	Run Number	Sintered Weight Gain (mg/cm^2) and Thickness (10^{-3} Inch)	Silicided Weight Gain (mg/cm^2) and Thickness (10^{-3} Inch)	Silicon Modifier Atomic Ratio	Oxidation Results			
					1600°F		2400°F	
					Life (hrs)	Average Weight Gain (mg/cm^2)	Life (hrs)	Average Weight Gain (mg/cm^2)
NS-19 41.5Mo41.5W 15V2Fe	57	66.9/5.3	51.9/4.6	2.8	3 > 209	3.6	3 > 209	5.4
NS-20 42Mo42.5W 15V0.5B	58	77.7/6.2	51.4/4.4	2.3	3 > 209	4.3	3 > 209	6.0
NS-21 68Mo20W 5Ti5V2Fe	59	66.8/4.8	44.2/3.8	2.2	3 > 209	2.3	3 > 209	2.8
NS-22 69.5Mo20W 5Ti5V0.5B	60	66.4/4.8	43.3/3.8	2.2	3 @ 20	-	3 > 209	3 7
NS-23 15Mo63W 15Ti5V2Fe	61	71.9/4.0	41.0/3.8	2.2	3 > 209	1.9	3 > 209	3.1
NS-24 15Mo64.5W 15Ti5V0.5B	62	60.5/4.1	37.8/3.5	2.3	3 @ 2	-	3 > 209	4.0

(A) Vanadium having approximately 0.5% oxygen added as hydride.
(B) Titanium added as hydride.

Series V

The oxidation testing of Series V coatings on FS-85 was conducted in the same manner described in Section 3.3.1. The test results listed in Table XV and displayed in Figures 28 and 29 show consistently good performance for all coatings except NS-23. The iron addition resulted in liquid phase sintering which caused an increased amount of titanium to be retained by the substrate. This increased titanium retention, coupled with the low vanadium content of NS-23, produced coatings that developed 1600° F failures of the type shown in Figure 29. All coatings, including NS-23, afforded excellent protection at 2400° F.

TABLE XV

COATING APPLICATIONS AND FURNACE OXIDATION TEST RESULTS ON COATED FS-85

Modifier Alloy (A) (B)	Run Number R-( )	Sintered Weight Gain (mg/cm^2) and Thickness (10^{-3} Inch)	Silicided Weight Gain (mg/cm^2) and Thickness (10^{-3} Inch)	Silicon Modifier Atomic Ratio	Oxidation Results			
					1600°F		2400°F	
					Life (hrs)	Average Weight Gain (mg/cm^2)	Life (hrs)	Average Weight Gain (mg/cm^2)
NS-3 35Mo35W20Ti10W	64	52.6/4.3	37.9/3.5	2.2	3 > 209	2.1	3 > 209	2.9
NS-4 15Mo65W15Ti15V	65	56.0/4.6	38.6/3.5	2.3	3 > 209	2.5	3 > 209	3.3
NS-15 15Mo65W15Ti5V	63	65.7/4.2	37.6/3.3	2.2	3 > 209	2.5	3 > 209	3.1
NS-1 35Mo35W15Ti15V	66	51.7/4.2	38.4/3.5	2.3	3 > 209	2.9	3 > 209	3.3
NS-23 15Mo63W15Ti5V2Fe	67	71.6/4.3	40.7/3.6	2.1	2, 20, 121	-	3 > 209	3.0

(A) Vanadium having approximately 0.5% oxygen used.
(B) Titanium added as TiH_2

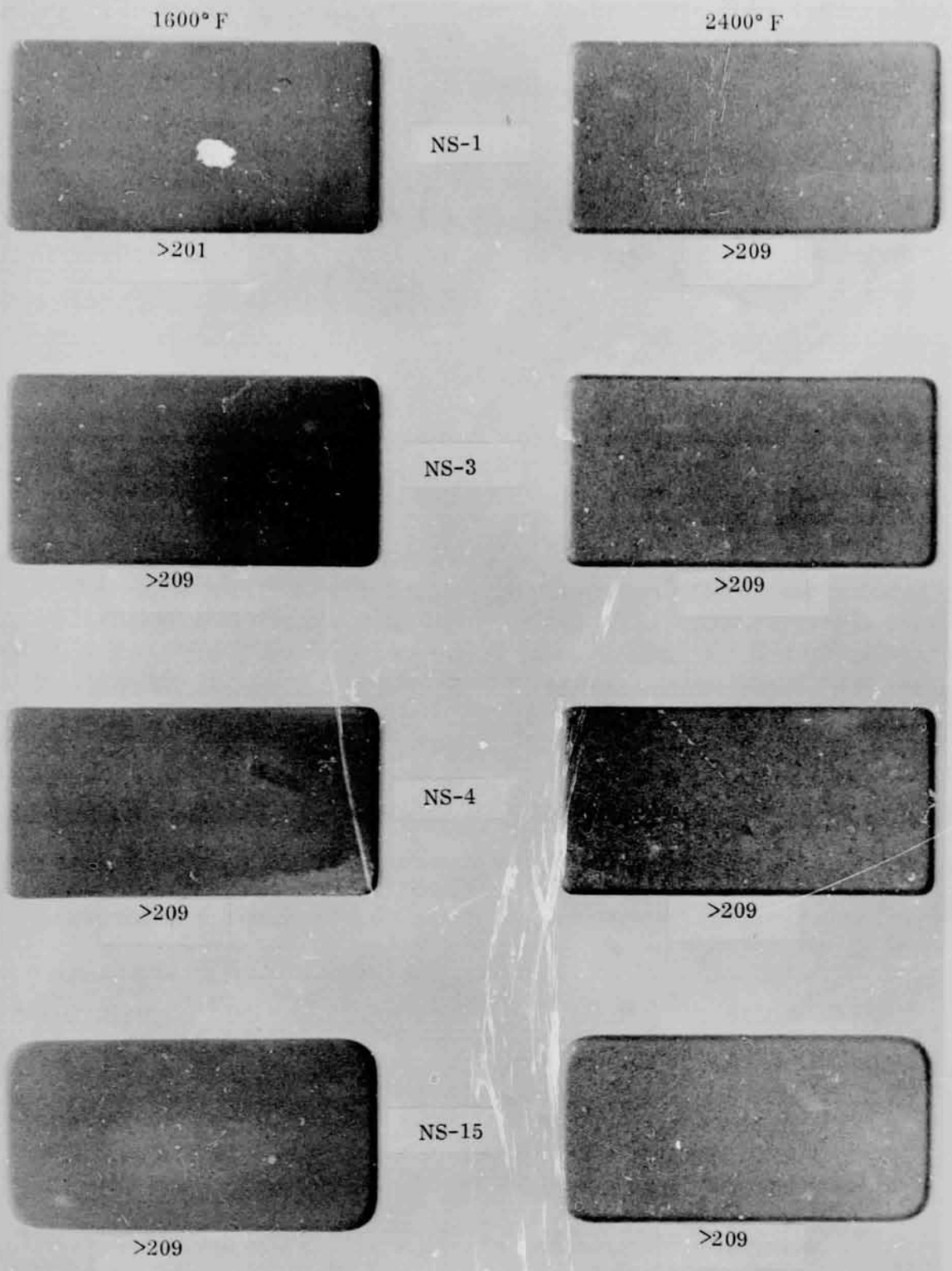


FIGURE 28. COATED FS-85 SPECIMENS AFTER FURNACE OXIDATION TESTING AT 1600° F AND 2400° F

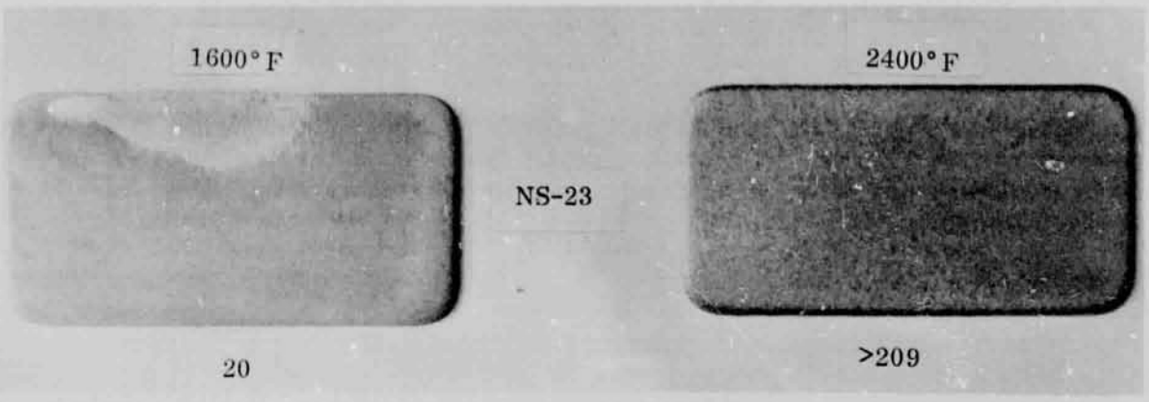


FIGURE 29. COATED FS-85 SPECIMENS AFTER FURNACE OXIDATION TESTING AT 1600° F AND 2400° F

3.3.3 Bend Testing

To assess the extent of substrate embrittlement after coating and also after oxidation exposure, room temperature bend testing was performed on a single specimen of each coating. The test method is covered in Section 3.3.1. A typical plot of ram load versus ram travel is shown in Figure 30. The initial sharp drop in the load was coincident with the compressional shear failure of the coating adjacent to the ram. Although the bend angles can be measured quite accurately, an uncertainty of approximately 5 degrees existed for the angle at which detectable cracks appeared in the substrate.

All as-coated and all 200-hour oxidation tested specimens had considerable ductility considering the severity of the 1t radius bend. The results of the tests on both T222 and FS-85 are listed in Table XVI. The specimens oxidized at 2400° F tended to be slightly more ductile than those in the as-coated condition or as-oxidized at 1600° F.

No general correlations could be made between bend angle at failure and composition. Both high titanium, e.g., NS-1, -2, -3, -4 and low titanium, e.g., NS-9 (none) and NS-10 modifiers retained excellent ductility in the substrate.

3.3.4 Ballistic Impact Plus Oxidation Test Results

The coatings that were found to be satisfactory in oxidation testing were further evaluated by ballistic impact as described in Section 3.3.1.

Photographs of representative coatings on T222 after the condition 1 (170 $\pm$ 15 ft/sec) impact are shown in Figure 31. This figure shows that the NS-5 coating was considerably more impact-sensitive than NS-1. Cracks appeared on the back side of specimens of all coating compositions (barely visible in Fig. 31). Occasionally the

TABLE XVI

BEND ANGLES OF T222 OR FS-85 WITH VARIOUS NS SERIES COATINGS BEFORE AND AFTER 200-HOUR OXIDATION

Modifier Alloy	Substrate	Atomic Ratio Silicon Modifier	Bend Angles (R = 1t) Degree					
			As-Silicided		1600°F Oxidation		2400°F Oxidation	
			Crack Substrate	Fail	Crack Substrate	Fail	Crack Substrate	Fail
NS-1	T222	2.3	73	>95	75	>95	>95	>95
NS-2	T222	2.3	91	>95	84	>95	68	95
NS-3	T222	2.3	80	>95	85	>95	83	>95
NS-4	T222	2.0	77	92	76	>95	>95	>95
NS-5	T222	2.2	62	91	73	95	>95	>95
NS-6	T222	2.7	53	84	52	>95	>95	>95
NS-7	T222	2.3	85	>95	61	91	>95	>95
NS-8	T222	2.4	74	93	92	>95	>95	>95
NS-9	T222	2.5	67	>95	82	95	79	>95
NS-10	T222	1.9	93	>95	74	>95	95	>95
NS-11	T222	3.2	95	>95	>95	>95	>95	>95
NS-12	T222	3.1	95	>95	>95	>95	>95	>95
NS-13	T222	3.3	95	>95	Oxidation Failed	-	>95	>95
NS-14	T222	2.6	60	72	56	65	50	68
NS-15	T222	2.2	38	72	55	66	48	>95
NS-16	T222	2.6	42	>95	58	71	>95	>95
NS-17	T222	2.4	62	76	58	71	82	>95
NS-18	T222	2.1	42	68	42	70	88	>95
NS-19	T222	2.8	60	70	49	61	83	>95
NS-20	T222	2.3	50	60	57	61	90	>95
NS-21	T222	2.2	50	71	78	95	78	>95
NS-22	T222	2.2	95	>95	Oxidation Failed	-	>95	>95
NS-23	T222	2.2	70	86	48	91	88	>95
NS-24	T222	2.3	46	76	Oxidation Failed	-	95	>95
NS-10Fe	T222	2.1	92	>95	>95	>95	>95	>95
NS-1	FS-85	2.3	80	>95	>95	>95	80	>95
NS-3	FS-85	2.2	95	>95	>95	>95	>95	>95
NS-4	FS-85	2.3	65	82	84	95	>95	>95
NS-15	FS-85	2.2	95	>95	>95	>95	>95	>95
NS-23	FS-85	2.1	82	>95	Oxidation Failed	Oxidation Failed	>95	>95

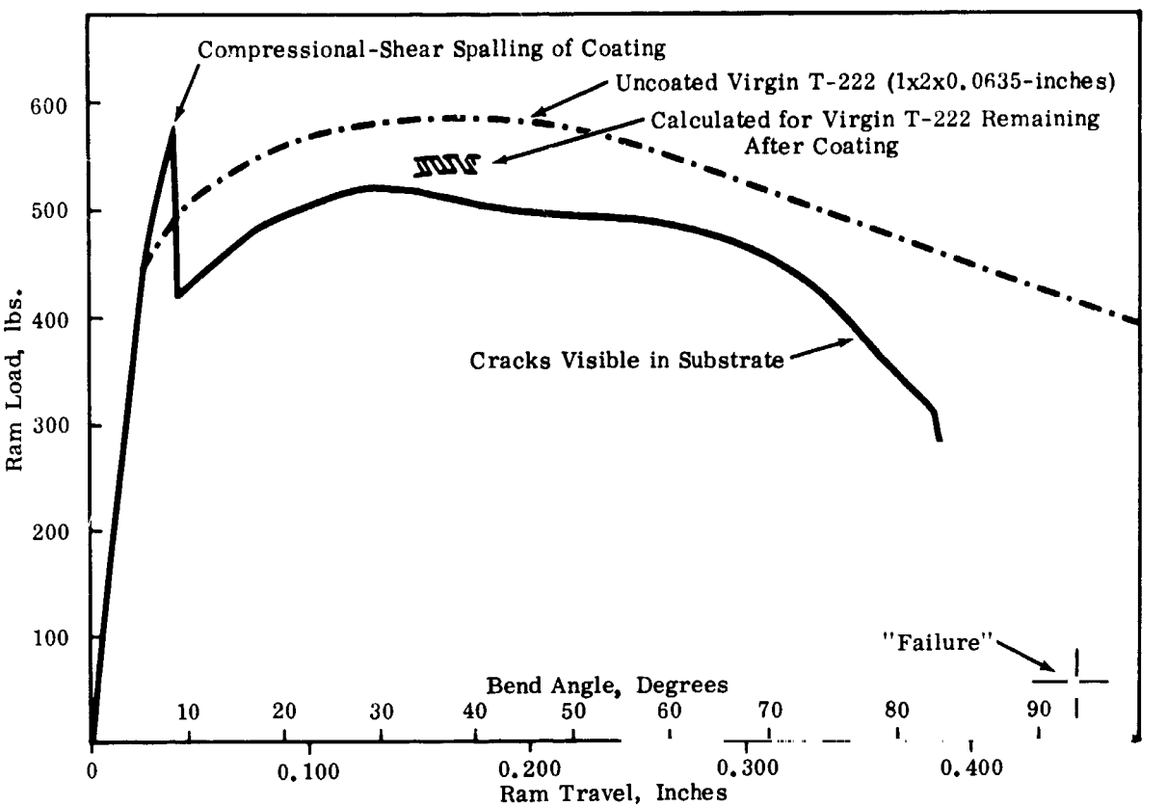


FIGURE 30. REPRESENTATIVE BEND TEST DATA PLOT FOR COATED T222

cracks intersected, allowing small pieces of coating to fall out. Photographs of a typical coating on FS-85 after the condition 1 impact and 20 hours of cyclic oxidation at 2400° F are shown in Figure 32. The impact caused considerably less permanent damage to coated FS-85 than T222.

Figure 33 shows damage resulting from condition 2 impact (240 ft/sec) at room temperature. On the impact side, the coating was forced into the substrate with "cleavage" (resembling compressive shear) occurring around the impact point. On the reverse side of the 0.060-inch thick specimen, cleavage occurred over an area comparable in size to the front face damage.

Damage resulting from impacting the specimens at 1600° F is shown in Figure 34. The nature and extent of damage to the back side of specimens for all chemistries except NS-23 on T222 was essentially as shown for NS-1 in Figure 34. One specimen each of NS-2, -6, and -10, and both specimens of NS-9 showed coating "pop off". Both specimens of NS-23 survived 10 hours and were the only T222 specimens tested with condition 2, 1600° F impact. In all cases the effect of condition 1 damage was far more severe at 1600° F than at room temperature.

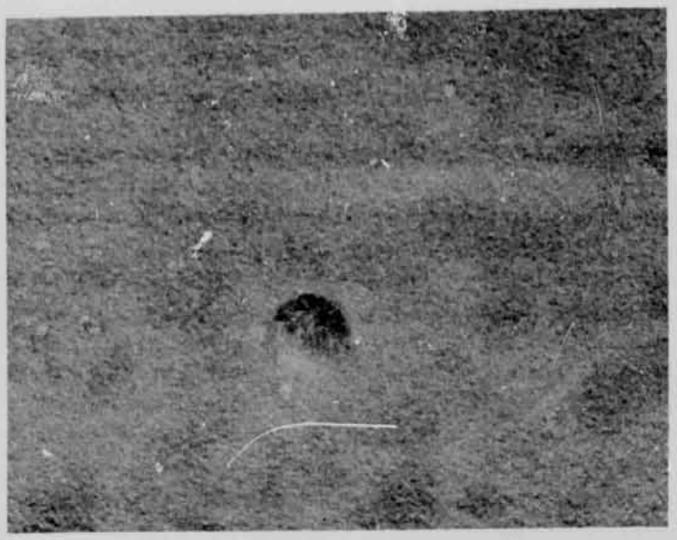
T222 ALLOY

NS-5
Impact Side

NS-1
Impact Side
(Typical of all 10 coatings
except NS-5)

NS-1
Back Side
(Typical of all 10 coatings)

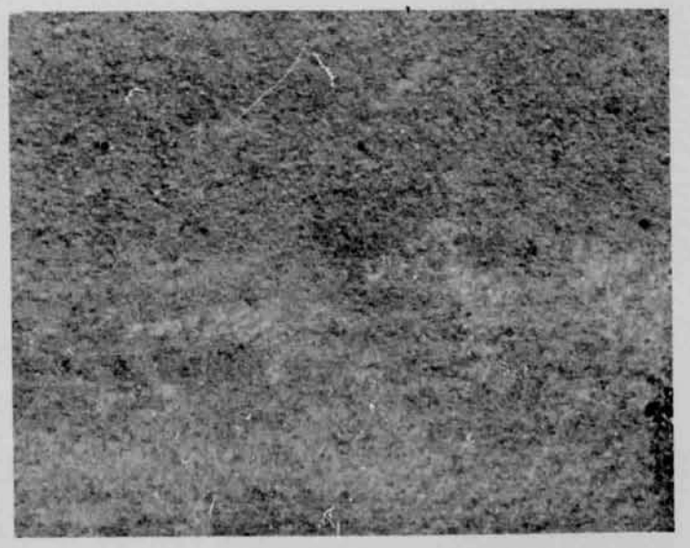
FIGURE 31. SPECIMENS AFTER INITIAL ROOM TEMPERATURE IMPACT AT CONDITION 1 (0.44 gm ball at 170 ± 15 ft/sec)



FS-85 ALLOY

NS-1
Front Side
(Typical of all 5 coatings tested)

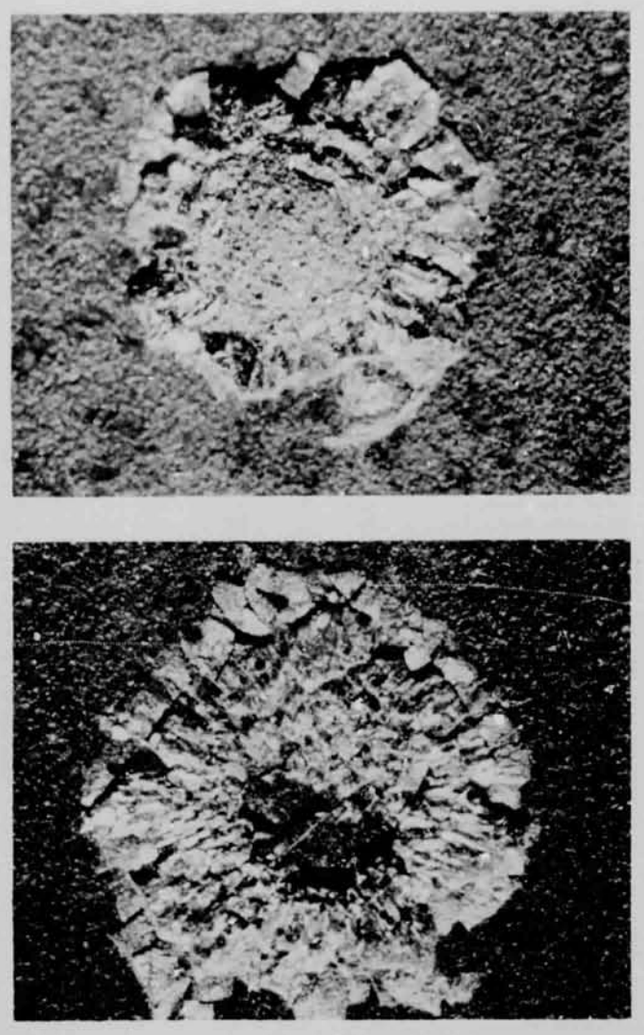
Magnification: 6X



Back Side

Magnification: 6X

FIGURE 32. SPECIMEN AFTER INITIAL ROOM TEMPERATURE IMPACT AT CONDITION 1 FOLLOWED BY 20 HOURS OF CYCLIC 2400° F OXIDATION



T222 ALLOY

Front Side

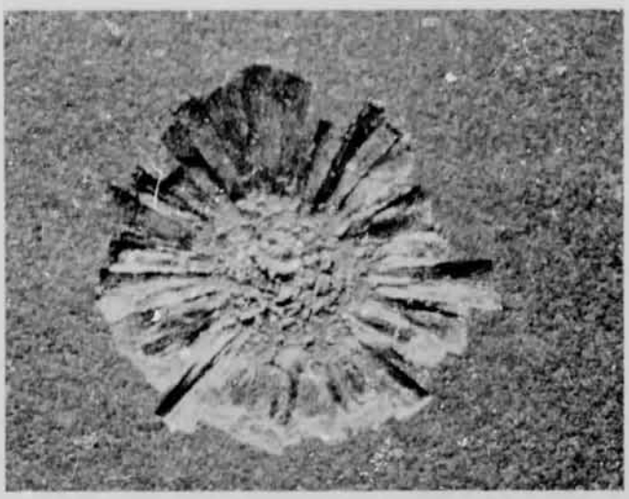
NS-1
(Typical of all 10 coatings)

Back Side

Magnification: 14X

FIGURE 33. SPECIMENS AFTER SECOND ROOM TEMPERATURE IMPACT (CONDITION 2) PRECEDED BY 10 HOURS OXIDATION (0.44 gm ball at 240 ± 40 ft/sec.)

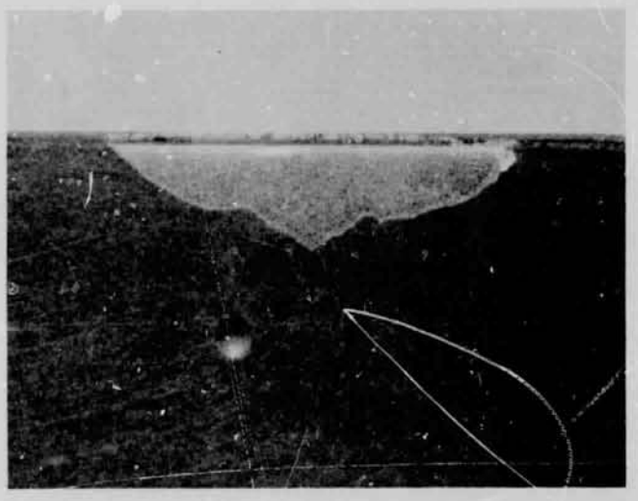
The observation that back-side damage under impact condition 1 was much greater at 1600° F than at room temperature caused concern that this might be due to either a change in the properties of the coating system or to a change in the method of fixturing the specimen. In a separate test an undamaged specimen, placed in the Inconel fixture (Fig. 23) which characteristically held the sample loosely by both ends, was impacted at room temperature. The back-side damage was virtually identical to that for specimens held by one end in the aluminum clamp.



T222 ALLOY

NS-1
Typical of back side of all
NS-1 through NS-10 coatings

Magnification: 10X



NS-9
Showing coating "pop-off"
running to edge.

Magnification: 3X

NS-1
Impact Side

Magnification: 10X

FIGURE 34. SPECIMENS IMPACTED AT 1600° F AT CONDITION 1
(0.44 gm ball, 170 ± 15 ft/sec.) BEFORE OXIDATION

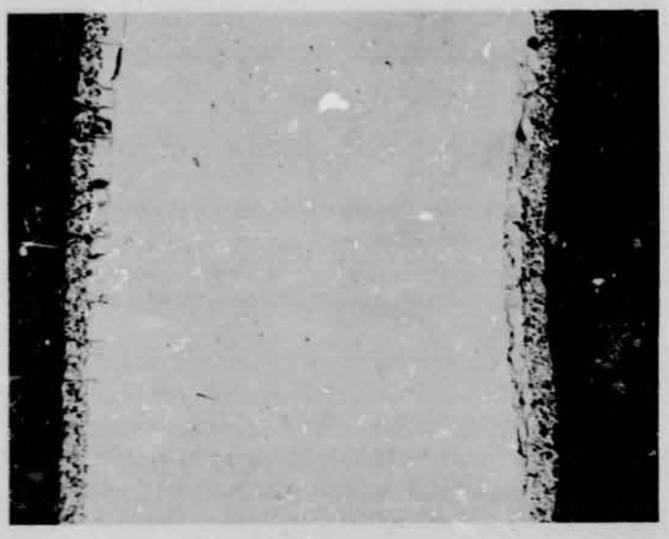
Figures 35 and 36 show the metallographic effects of condition 1 room temperature impact on coated FS-85 and subsequent oxidation testing. The coatings demonstrated the ability to sustain significant impact damage while continuing to provide oxidation protection for up to 20 hours at 1600° F or 2400° F. The coatings were fractured by the impact, but remained adherent to the considerably deformed substrate. The shock wave produces cracks indicating tensile fracture normal to the wave front on the side opposite the point of impact.

Figure 37 shows metallographically the effect on coated FS-85 of condition 1 impact at 1600° F and subsequent 1600° F oxidation. Note the significant difference in coating cleavage relative to that observed for coatings on T222 (Fig. 34). This difference in coating retention supports the assumption that additional coating-substrate interdiffusion and bonding could improve post impact oxidation life.

In conclusion it is noted that the ability of the silicide coatings to withstand impact is significant, but the levels of impact are considered to be modest by jet engine impact damage standards (where 600 to 800 ft/sec might be encountered).

Oxidation Test Results After Impact

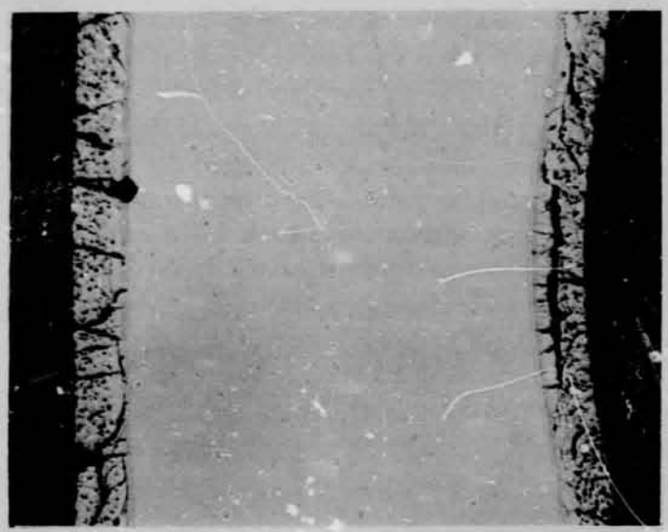
The results of the oxidation tests following impact of coated T222 specimens are displayed graphically in Figure 38. There was no significant trend in oxidation resistance for coated T222 specimens impacted at room temperature and tested at either 1600° F or 2400° F. Specimens impacted at 1600° F, however, show a strong relationship between failure time and atomic percent titanium in the coating modifier, as is shown in Figure 39. The two-hour failures usually corresponded to failure on the impact side and were associated with coating delamination due to substrate oxidation. Failure on the back side proceeded at a somewhat more constant rate with oxide growth initiating in the crater. The rate of oxide growth was appreciably faster for coatings NS-7 through NS-17 (zero to 11 atomic percent titanium) than for NS-1 through NS-6 (titanium equal to 18 to 36 atomic percent). A comparison of results for NS-4 and NS-1 suggested that a tungsten-to-molybdenum weight ratio greater than 1 was desirable to improve impact resistance; however examination of the data in Figure 39 indicated that the modifier coating (if sintered 15 hours at 2760° F) must contain >25 atom percent titanium prior to sintering to produce a coated T222 specimen that will



Room Temperature Impacted at Condition 1.
Oxidation Tested at 1600° F for 20 Hours.
(See Fig. 40)

Magnification: 40X

FIGURE 35. FS-85 SUBSTRATE COATED WITH NS-1 - OXIDATION AFTER BALLISTIC IMPACT



Room Temperature Impacted at Condition 1.
Oxidation Tested at 2400° F for 20 Hours
(See Fig. 40)

Magnification: 40X

FIGURE 36. FS-85 SUBSTRATE COATED WITH NS-3 - OXIDATION AFTER BALLISTIC IMPACT

Impacted at 1600° F at
Condition 1.
Oxidation Tested at 1600° F
for 20 Hours.
(See Fig. 40)

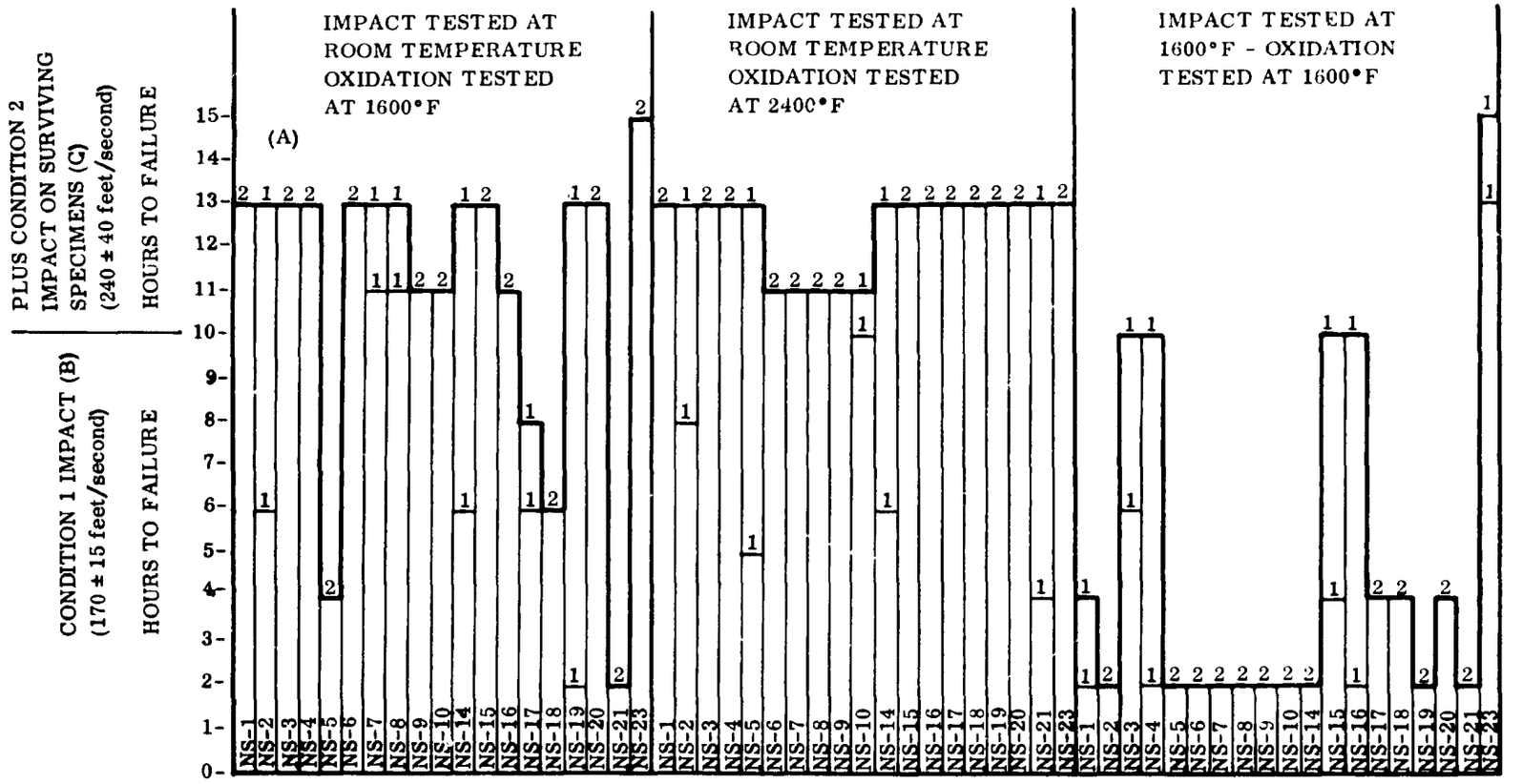
Magnification: 40X

FIGURE 37. FS-85 SUBSTRATE COATED WITH NS-23 - OXIDATION AFTER BALLISTIC IMPACT

survive more than 2 hours at 1600° F after 1600° F impact. A comparison of NS-4 (20Mo50W15Ti15V), NS-1 (35Mo35W15Ti15V) and NS-5 (50Mo20W15Ti15V) provides an example of this effect. The samples coated with NS-5 (25 atomic percent titanium) both failed in the first 2 hours at 1600° F after 1600° F impact while those coated with NS-1 (27 atomic percent titanium) survived 2 and 4 hours, and those coated with NS-4 (29 atomic percent titanium) survived 2 and 10 hours. Variation of the W/Mo ratio showed no measurable trend when the atomic percent titanium was maintained at a constant level.

The results of the oxidation tests following impact of coated FS-85 specimens are shown in the bar graph in Figure 40. In all cases the life after impact is greater for coated FS-85 than for T222. All coatings on FS-85 withstood oxidation to 10 hours in condition 1 even when impacted at 1600° F. On T222, only NS-23 survived in oxidation testing for 10 hours after being impacted under condition 1 at 1600° F.

Although the bar graph in Figure 40 shows significant life for all coatings after condition 2 impact, it should be noted that front and back cleavage, similar to that shown in Figure 33, occurred. The major difference between the substrates was the retention of an alloy layer on the surface of FS-85 which provided short-term oxidation protection. Although the majority of the coatings survived for the duration of the test (10 hours after condition 2 impact), it is unlikely that any samples would have survived more than an additional 10 hours of testing. In all cases a white oxide was being slowly generated in the impacted regions indicating the formation of substrate oxide.



A. Number indicates specimens failing at the particular time.

B. Two-hour cycles to 10 hours

C. After ballistic impact of B specimen surviving 10 hours, specimens were furnace oxidized for one 1-hour, two 2-hour, and one 5-hour cycles.

D. Impacting was effected with a Crossman Model 160 air rifle using 3/16-inch chromium steel balls (0.44 gms) and nitrogen as the propellant gas.

FIGURE 38. BALLISTIC IMPACT-OXIDATION TEST RESULTS FOR COATED T222 (D)

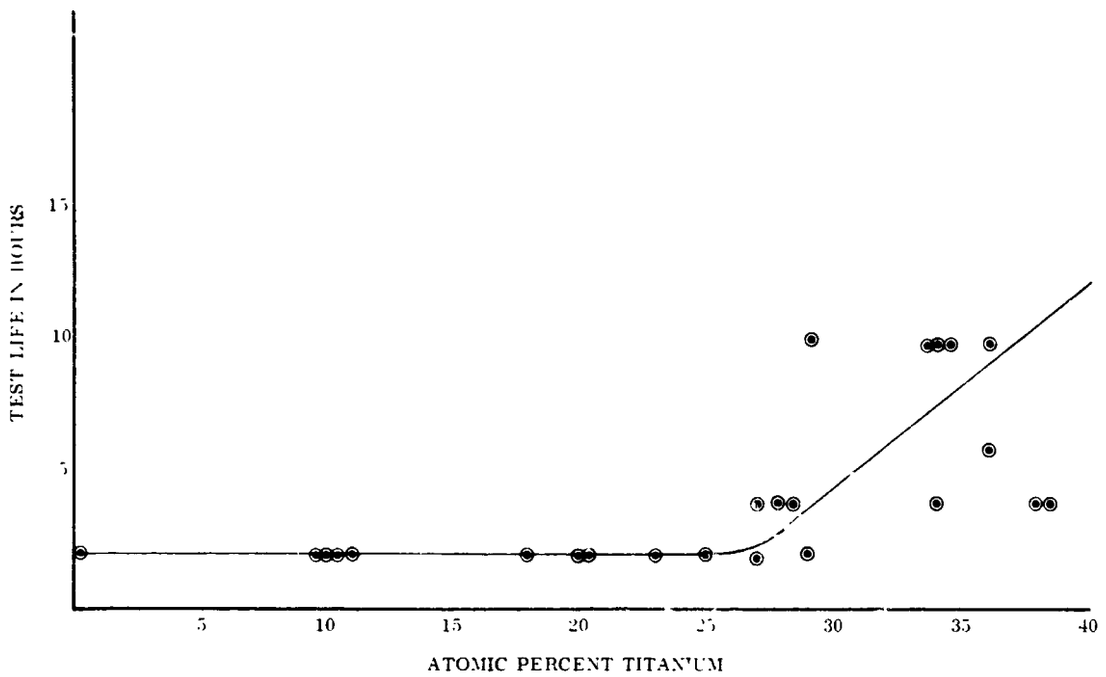


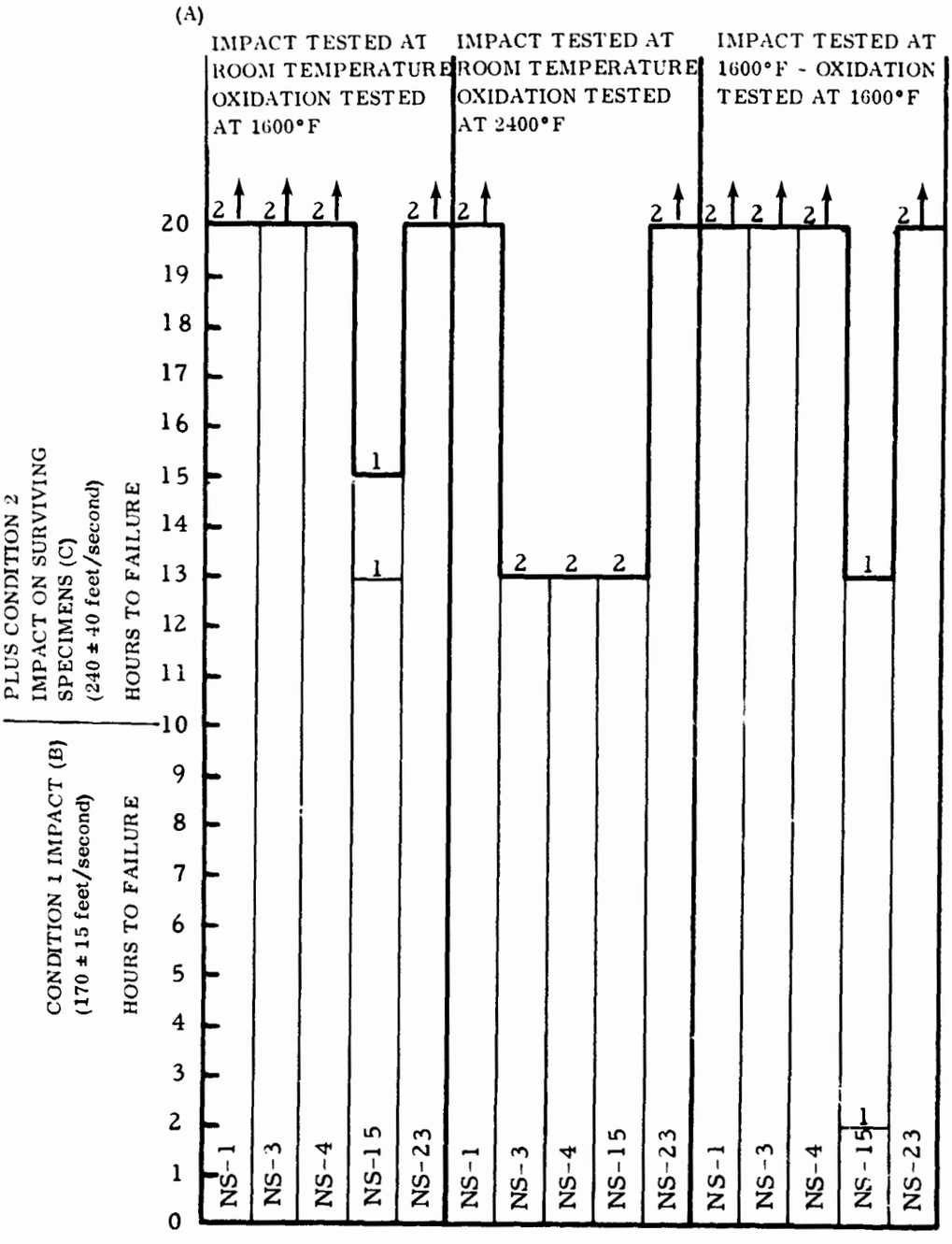
FIGURE 39. RELATIONSHIP OF TEST LIFE AT 1600° F AFTER CONDITION 1 IMPACT AT 1600° F TO TITANIUM CONTENT FOR COATINGS WITH MODIFIER VACUUM SINTERED 15 HOURS AT 2760° F ON T222

3.3.5 Torch Test Results

Standard 1-inch by 2-inch coated specimens of the type utilized for oxidation, bend testing, and impact were used for torch testing. These specimens were all prepared with low oxygen modifier materials including titanium hydride. The experimental procedure was described in Section 3.3.1.

Performance of the coated specimens in the torch test was rated on the following arbitrary scales: (1) severe failure, (2) moderate failure, (3) incipient failure, and (4) no failure (higher rating number corresponds to greater resistance). Figure 41 shows typical specimens of each of the three failure levels. Results of the torch tests are summarized in Table XVII.

The greatest protection in torch testing was afforded by coatings NS-4 and NS-7 to NS-10. The NS-4 coating is characterized by a high tungsten-to-molybdenum ratio which results in reducing the retention of titanium in the modifier (Sec. 3.5.1).

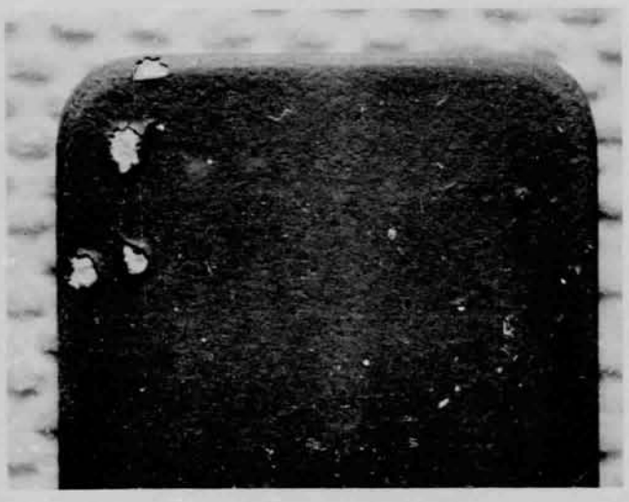


(Same Notes as Figure 38)

FIGURE 40. BALLISTIC IMPACT-OXIDATION TEST RESULTS FOR COATED FS-85 (D)

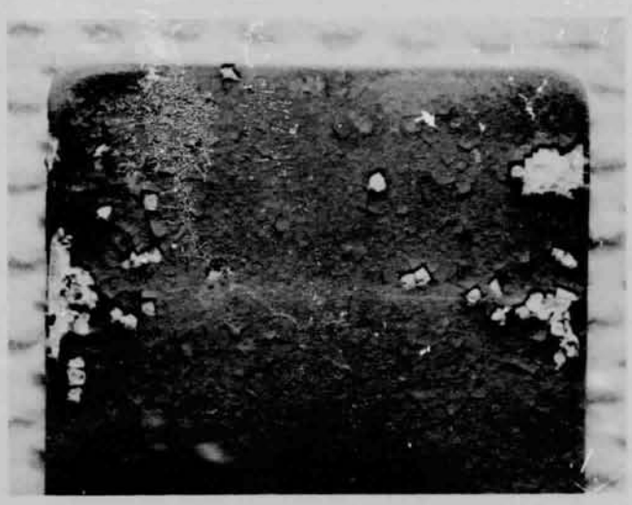
"3-Incipient Failure"

NS-1
Specimen Torch Tested at
2640 F, Flame Side



"2-Moderate Failure"

NS-3
Specimen Torch Tested at
2640 F, Back Side



"1-Severe Failure"

NS-5
Specimen Torch Tested at
2640 F, Flame Side

Magnification: 3X

FIGURE 41. REPRESENTATIVE TORCH TEST SPECIMENS

TABLE XVII

RESULTS OF TORCH TESTING SILICIDED COATINGS

Key: 1 - Severe Failure
2 - Moderate Failure
3 - Incipient Failure
4 - No Failure

Note: Turntable rotated at 0.25 rpm for a 10-hour period, with each specimen in the hot zone approximately 7 percent of the test period.

Modifier Alloy	Test 1 2530° F	Test 2 2640° F	Test 3 2685° F	Row Total
NS-1 35Mo35W15Ti15V	4	3	2	9
NS-2 35Mo35W10Ti20V	2	4	3	9
NS-3 35Mo35W20Ti10V	4	2	2	8
NS-4 20Mo50W15Ti15V	4	4	4	12
NS-5 50Mo20W15Ti15V	4	1	2	7
NS-6 40Mo40W10Ti10V	3	4	3	10
NS-7 45Mo45W5Ti5V	4	4	4	12
NS-8 40Mo40W5Ti15V	4	4	4	12
NS-9 42.5Mo42.5W15V	4	4	4	12
NS-10 70Mo20W5Ti5V	4	4	4	12

The remaining coatings (NS-7 to -10) are characterized by a low initial titanium content (zero to 5 weight percent titanium). The poorest performing coating was NS-5, which was characterized by high molybdenum/tungsten ratio which results in a high retention of the initial 15 percent titanium in the coating. The high titanium content in the coating-substrate combination generally resulted in formation of oxide at the base of coating fissures which ultimately results in coating spall of the type shown for NS-5 in Figure 41.

3.3.6 Discussion of Test Results and Selection of Compositions for Final Screening

The results of 200-hour furnace oxidation testing appear to be of somewhat limited value in differentiating between the 26 coatings, particularly when it is realized that NS-7, NS-8 and NS-10, which showed early failures, might have been improved by the use of titanium hydride in the same way that NS-6 was improved. The NS-11, NS-12 and NS-13 compositions, sintered 1.5 hours at 2200° F instead of the standard 15 hours at 2760° F, were unsatisfactory; but the indications are that this was the result of excessive vanadium and titanium retention which would not have been retained if the modifier had been vacuum sintered for 15 hours at 2760° F.

The coatings (particularly those with a high W/Mo ratio) used to evaluate iron as a substitute for vanadium were found to be unsatisfactory in low-temperature (1600° F) oxidation. This emphasized the value of vanadium in combating pest type (1600° F) failures.

The results of bend testing were in no way discriminating in that all specimens tested had good ductility.

The results of the ballistic impact-oxidation tests, particularly those involving impact at 1600° F, tended to be somewhat less than fully quantitative to the extent that the degree of visible coating damage was not consistently reproducible. In all cases, both the initial and the as-oxidized damage to T222 was more severe than with the same coating applied to FS-85.

The major conclusion was that after 1600° F impact, the resistance to 1600° F oxidation improved as the atomic percent of titanium increased for coatings applied with a 15-hour, 2760° F vacuum sinter of the modifier. This improved life expectancy was further enhanced by the addition of Fe to the modifier (NS-23). This increeased life after impact is the result of two effects: (1) iron and titanium additions increase modifier sintering, thus improving coating strength and coating-to-substrate bonding; (2) titanium diffusion into the substrate improves the short-term oxidation resistance so that even after the coating is lost, due to impact, the alloyed substrate will survive several hours before severe oxidation damage occurs.

It is apparent that the majority of the chemistries were sufficiently promising to warrant further consideration. The tests to which the coatings were subjected were not sufficiently discriminating to single out any single system as being superior to the others. Due to this lack of discrimination, the program was modified at this point to include high-temperature, oxidation-erosion testing. The coatings selected for evaluation on T222 included all of the original ten except NS-8, deleted only because of its similarity to NS-6. The coating NS-10 Fe was included because it was the only vanadium-free chemistry to survive 1600° F oxidation for 200 hours. Also included were the most promising coatings with maximum W/Mo ratio NS-15, -16, -17 and -18. Of the coatings utilizing iron as a sintering aid, NS-23 was included due to its superior performance in impact.

In addition to these chemistries for T222, four were selected for evaluation on FS-85. They were NS-1, NS-3, NS-4 and NS-15. The principal reasons for their selection were:

- NS-1 - Excellent performance and serves as a standard
- NS-3 - Survived 1600° F oxidation even when prepared with high oxygen content vanadium
- NS-4 - Superior coating with high W/Mo ratio
- NS-15 - Modification of NS-4 which performed exceptionally well on T222

3.4 FINAL SCREENING

The basis for the direction of the later portion of the program was the need for more discriminating tests to allow selection of the best coating-substrate systems. The furnace cyclic oxidation tests, conducted for 200 hours on 26 chemistries at 1600 and 2400° F, did not resolve any significant differences between the various coatings. Because the potential application of the coated alloys is in turbine vanes, a test more closely simulating this environment was desired. Oxidation-erosion rig testing is currently in favor for screening turbine vane and blade materials. It provides a high mass flow at near sonic velocities, rapid specimen up-shock and down-shock, erosion by carbon particles and a severe thermal gradient on the specimen. All are conditions that turbine vanes experience in service. The program was redirected to include: (1) erosion rig testing of the promising compositions developed in the program; (2) slow cycling of selected coatings to isolate low-temperature problems; and (3) development and testing of coating modifications to improve low-temperature performance. The program also retained, as originally planned, 800-hour - 2400° F oxidation exposure and the mechanical testing of both T222 and FS-85 both before and after 800-hour oxidation exposure.

3.4.1 Test Techniques

Furnace Oxidation

The 800-hour cyclic furnace oxidation testing was conducted utilizing the same equipment described in Section 3.3.1, Furnace Oxidation. Cyclic oxidation of the silicided specimens was accomplished at 2400° F for two 40-hour cycles during the work week and for 65 hours over the weekend. The weight change of the specimens was monitored by weighing each sample before and after each 65-hour weekend cycle. The specimen configuration was a tensile type shown in Figure 42.

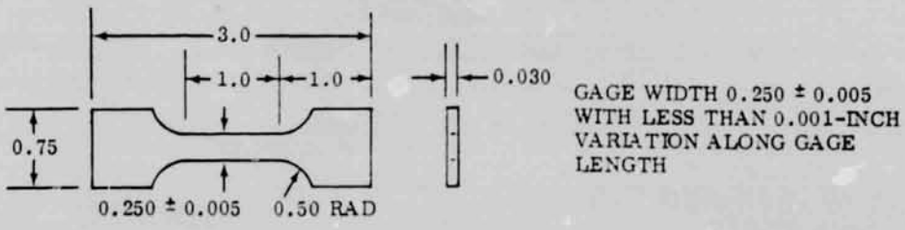


FIGURE 42. INSTRON MODEL TT-D TESTING MACHINE AND TENSILE TEST SPECIMEN

After completion of 800 hours of oxidation, a section was cut from the grip portion of one specimen of each coating-substrate combination. The specimen was utilized for metallographic and microprobe evaluations.

Electron Beam Microprobe Analyses

Since the electron beam microprobe analyzer was the major analytical tool utilized for chemical evaluation of program specimens, it is worthwhile to briefly discuss the experimental details. Pure metal standards of each element of the coating were included in the same metallographic mount as the coated specimens. Conventional polishing techniques with alumina and chromium oxide abrasives were used. After polishing, each specimen was lightly etched and ultrasonically cleaned to reduce the possibilities of material being smeared across neighboring phases. To determine six or more elements (Cb, Ta, W, Mo, V, Ti, Si), it was necessary to probe exactly the same area three times or more, and the problem of beam stability (point counting techniques) due to charging of the specimen surface or beam contact with poorly conducting phases was encountered. This problem was resolved by shadowing the surface of the specimen and mount with carbon (approximately 150 Å thick). In the evaluation of specimens in Reference 1, the continuous traverse method was used without ultrasonic cleaning or carbon shadowing.

The Norelco AMR III Electron Probe Microanalyzer, utilizing a 2-micron beam operating at 25 kilovolts, was used to analyze for the coating and substrate elements. The radiation from Si, Ti, Cb, Ta, W and Mo, was analyzed with the detectors in vacuum; whereas the detectors for the V analyses were in air at atmospheric pressure.

The data was processed by an IBM 360 computer using an EPMP-1 program. This program is designed to calculate the weight fraction of each element in a phase from the characteristic X-ray intensity measurements of the specimen and the standards. The program corrects for detector dead time, background, Philbert's absorption (Philbert's correction modified by those of Duncumb and Shields), and fluorescence (either Birk's, Castaing's or Reed's corrections). There is no correction provided in the program for the errors contributed by the following:

- Atomic number effect
- Fluorescence excitation by the continuum
- Contamination of the specimen or standard

Heinrick's Tables were used to obtain mass absorption coefficients and the Norelco Tables supplied the critical absorption energies.

Although the spot-probe technique eliminated errors due to the beam contacting phase boundaries, the shape of the analyzed particles might affect the analytical results. For instance, only the two-dimensional shape of a particular particle was known, and it is possible that the beam occasionally contacted a very thin particle and thus produced radiation from the underlying phase.

Mechanical Properties

Room temperature tensile tests to determine ductility and strength were performed on triplicate specimens in various stages of processing. Uncoated T222 and FS-85 alloys and modified plus silicide coated specimens were tested before and after 800 hours of cyclic oxidation exposure at 2400° F.

Cyclic oxidation of the specimens was accomplished as described in the preceding section, Furnace Oxidation. The room temperature tensile tests were performed using a Model TT-D Instron tensile testing machine shown in Figure 42. The test specimens for the measurement of mechanical properties were similar in design to the standard 1-inch gage length sheet stock tensile specimen shown in Figure 42. The 0.030-inch sheet material was used in the specimens. The specimens were deburred and radiused using a Sweco vibratory finisher prior to coating. The tests were conducted using a strain rate of 0.005 inch/inch/minute to 0.5 percent offset and at 0.05 inch/inch/minute until failure.

Slow Thermal Cycle Testing

The slow thermal cycle test rig was designed to produce a 1-hour cycle temperature profile with the temperature varying from a minimum of 850° F to a maximum of 2300° F and back to 850° F.

The profile test specimens (3/4 inch x 11 inches x 0.030 inch) were suspended in the unit and held in position by direct dead-weight loading through positioning grips.

The temperature profile is achieved by means of a preshaped temperature-time program cam, operating in conjunction with an electronic controller, magnetic modulator, and silicon-controlled rectifier. Test specimens are heated with twelve 500-watt, clear quartz tubular lamps enclosed in a water cooled, 3-1/2-inch diameter gold-plated reflector assembly. A thermocouple (Pt/Pt-13Rh) adjacent to the surface of the test specimen furnishes a feedback signal to the temperature control system. Deviation between specimen and program temperature was automatically corrected by regulations of the power to the quartz lamp heating unit. Temperature was recorded throughout the test period to indicate any deviation from the test program.

Oxidation/Erosion Tests

Oxidation/erosion rig tests were conducted on duplicate T222 or FS-85 alloy specimens with selected coatings. Test conditions were:

Temperature:	2400° F
Gas Velocity:	>2000 ft/sec (Mach 0.85)
Cycle:	1 hour in flame - 3 minutes air blast cool
Fuel:	JP-5
Oxidizer:	Air

The two Solar gas turbine environmental simulators (erosion rigs) are shown in Figure 43. Design details of these burners, Figure 44, are similar in features to those of Solar's modern small gas turbine combustors. A straight-through, can-type combustor is used with fuel atomization from a single nozzle. A water-cooled, 1-inch diameter, stainless steel nozzle is used for long-time, trouble-free operation. The flame tube is fabricated from Hastelloy X.

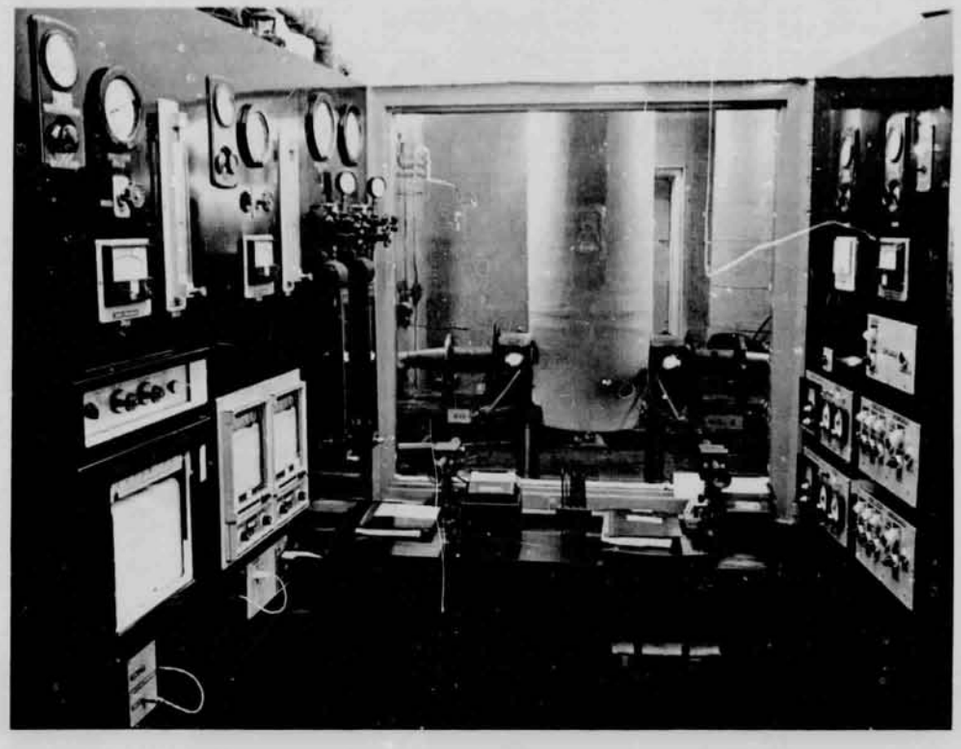
The control console for the two simulators is shown in Figure 43. Duplicate controls and measuring equipment are provided on the left side of the console for independent operation of each simulator. The major items used to ensure reproducible rig operation are:

- Fuel flow and pressure regulators
- Combustor pressure regulator and over-under temperature pyrometers
- Airflow orifice manometers
- Airflow reducing regulator controls

The two potentiometer-type recorders for measuring temperatures from the slip rings, the probe thermocouples, and the total radiation pyrometers are also located on this side of the console.

The main electrical control panels for each rig, the automatic recycling timer (60 minutes at temperature, 3 minutes cooling), and the fuel pump controls are all located on the right side of the control console.

A closeup of the two turbine environmental simulators is shown in Figure 43 (note the specimens in the hot gas stream). The total radiation pyrometers (Ircon Model 124PH) are located in the foreground of the photograph. These two pyrometers are focused on the hot specimens to monitor and record the temperature fluctuations throughout the tests. Once each hour the specimen temperature is manually checked by optical pyrometer readings. The specimen holder rotation motor, the slip-ring



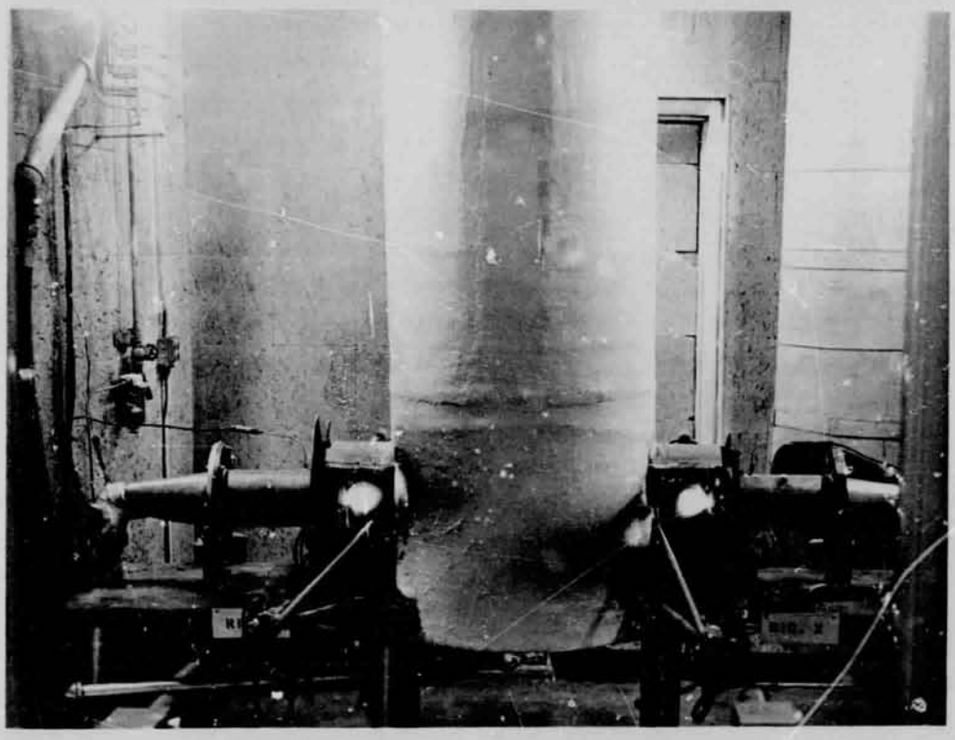


FIGURE 43. GAS TURBINE ENVIRONMENTAL SIMULATORS

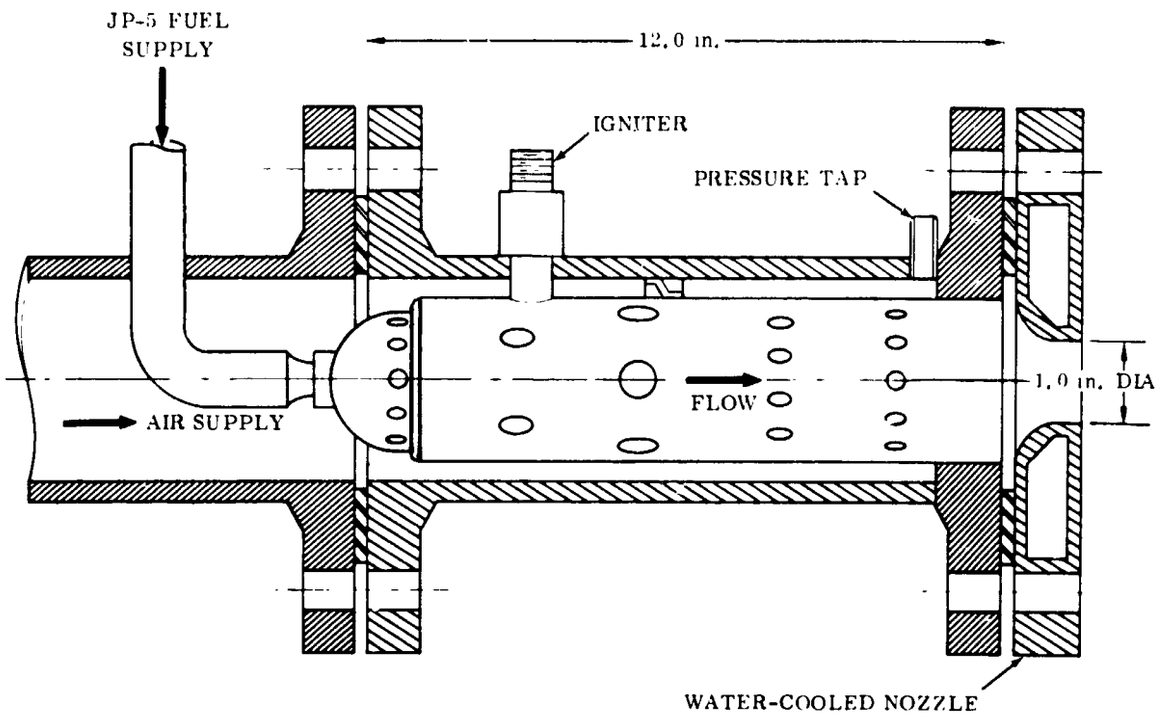


FIGURE 44. SOLAR ONE-INCH COMBUSTOR RIG

assembly, and the pneumatic piston that cycles the specimen holder-motor assembly in and out of the hot gas stream are not visible in the figures.

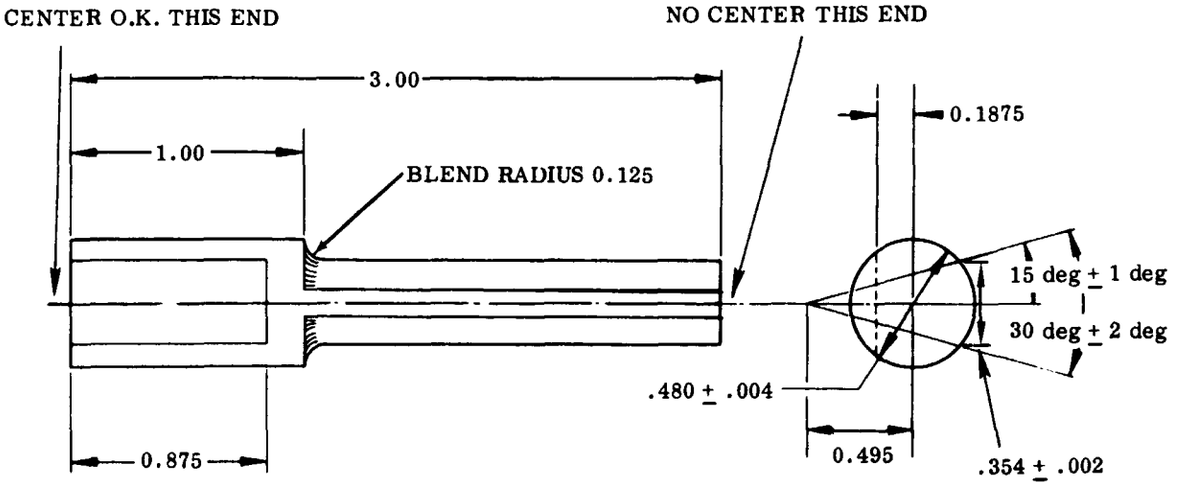
During the rig tests, eight specimens were mounted in a holder which rotated at 1725 rpm. Rotation in the gas stream is required to ensure that all specimens experience the same test environment. The holder is positioned so that the leading edge of the nearest specimen is 1 inch from the exit of the nozzle. The holder is fabricated from Inconel 718 alloy and the bolts are made from HS-25 alloy.

Temperature is the major parameter that must be carefully controlled to obtain quantitative, reproducible test results. In the rig tests, temperature is monitored by the total radiation pyrometer connected to a proportional band temperature controller recorder. The control of the specimen temperature is obtained by carefully adjusting and regulating the fuel flow to the combustor nozzle (air flow is held constant by means of dome loading, diaphragm-type, high-capacity, air regulators). Any deviation between the temperature setpoint and the specimen temperature is sensed in the temperature recorder-controller, which continuously activates an electric to-pneumatic converter thereby controlling a pneumatically operated fuel flow valve. Fuel flow is increased or decreased automatically as required to maintain the set temperature.

The temperature control was further verified by measurement of specimen metal temperature by means of a thermocouple inserted into a small hole in a test specimen. The hole was electrically discharge machined 2 inches deep through the base of the erosion bar so that the thermocouple tip would be in the center of the test section. The temperature was determined at the center of the test section to confirm the optical reading and at a depth of 1 inch to determine root radius temperature. Output of the thermocouple was fed into a Lebow Associates Model 6105-4 slip-ring assembly and then to a potentiometer-type strip chart temperature recorder.

Two specimens of each coating-substrate combination were prepared by machining the substrates, as shown in Figure 45, and coated by the standard modifier hand spray and pack cementation siliciding techniques.

A set of eight erosion bars were installed in the rotating specimen holder to permit four systems to be tested simultaneously with two specimens each. The burner was ignited and, when stable operation was achieved, the specimens were cycled into the hot gas stream. After approximately 30 minutes of operation, the holder was withdrawn and the lock bolts were again tightened. This was necessary to secure the erosion bars in the holder due to the high coefficient of thermal expansion of the holder relative to that of the specimens.



DIMENSIONS ± 0.010 INCH EXCEPT AS NOTED
FINISH /125 ALL OVER

FIGURE 45. WEDGE TEST SPECIMEN

Once each day the specimen holder was removed from the test rig and the specimens were examined visually. At the end of 100 hours of testing each specimen that had survived was removed from the holder for thorough examination. The specimens were then returned to test until failure. Removal of specimens from the holders and re-insertion may have increased the incidence of shank failures.

After failure, each specimen was removed from the holder, visually examined, photographed, and selected specimens were sectioned for metallography and microprobe analyses.

3.4.2 Furnace Testing

Selected coatings were evaluated on T222 and FS-85 alloys to determine both the oxidation protection provided over long periods (800 hours) at 2400° F and the effect of the coating and/or oxide penetration on the substrate mechanical properties. The coatings selected for evaluation of T222 were NS-3, -4, -15, and -23, while the FS-85 specimens were coated with NS-1 and NS-4. Standard techniques were used for application of the coatings. Cyclic oxidation of three specimens of each combination was accomplished as described in Section 3.4.1.

The specimens are shown in Figure 46 after 160 hours of oxidation. No sample had failed at that point in the test and all samples were of excellent appearance, exhibiting a glossy surface. After 227 hours of oxidation, a city-wide power failure caused the furnace to cool from 2400° F to 1400° F over a period of 5 hours. As a result of the slow cooldown, two samples of the NS-3 coating and one sample of the NS-15 coating failed on T222 substrates. On heatup, one sample of NS-23 on T222 failed. These slow-cooling failures, also noted in Reference 1, produced by either oxidation at the base of craze crack or nucleation and crystallization of the vitreous surface oxide. After a total of 391 hours of testing, the remaining samples had the excellent appearance shown in Figure 47. No further changes were noted at the completion of 800 hours of oxidation. The failures add support to the suspected importance of vanadium in these silicide coatings for protection of tantalum-base alloys. The coating NS-4, with no failures, was the coating containing the highest atomic percent vanadium tested in this series and probably, therefore, the greatest resistance to surface oxide crystallization.

The weight gain per unit area is plotted versus time in Figures 48 and 49. The plots are more nearly straight lines than parabolic, as one might expect. This deviation from parabolic oxidation would indicate that the primary mechanism is not diffusion controlled, but more likely the result of the thermocycling which opens microcracks during each cycle. Oxidation within the cracks prior to sealing may be large relative to the growth of oxide as a result of oxygen permeation or metal ion diffusion through the surface oxides. The low overall weight change and the shallow slope to the oxidation/time curve indicates a high oxidation resistance of this family of coatings.

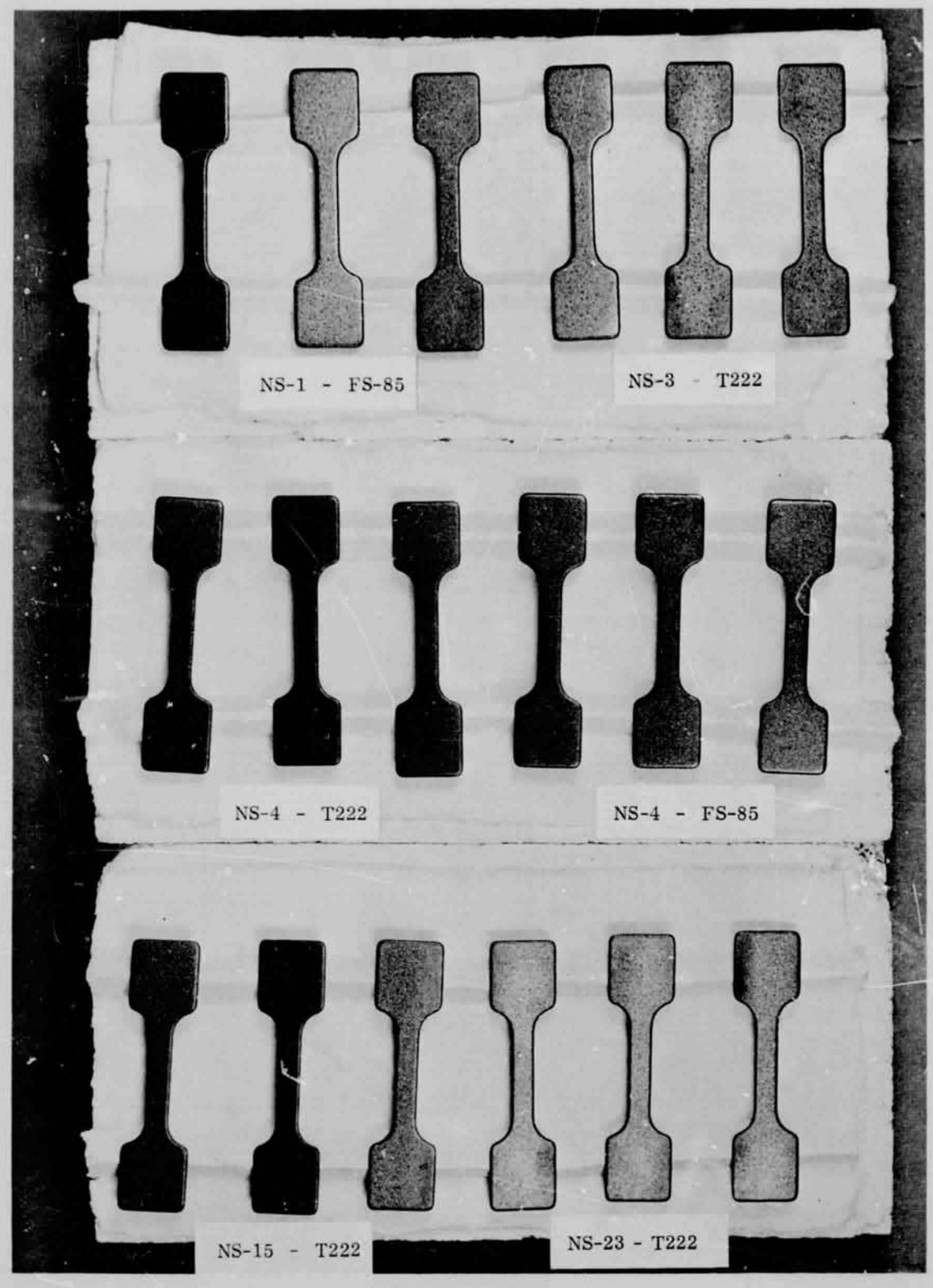


FIGURE 46. MECHANICAL TEST SPECIMENS FOLLOWING 160 HOURS OF CYCLIC OXIDATION

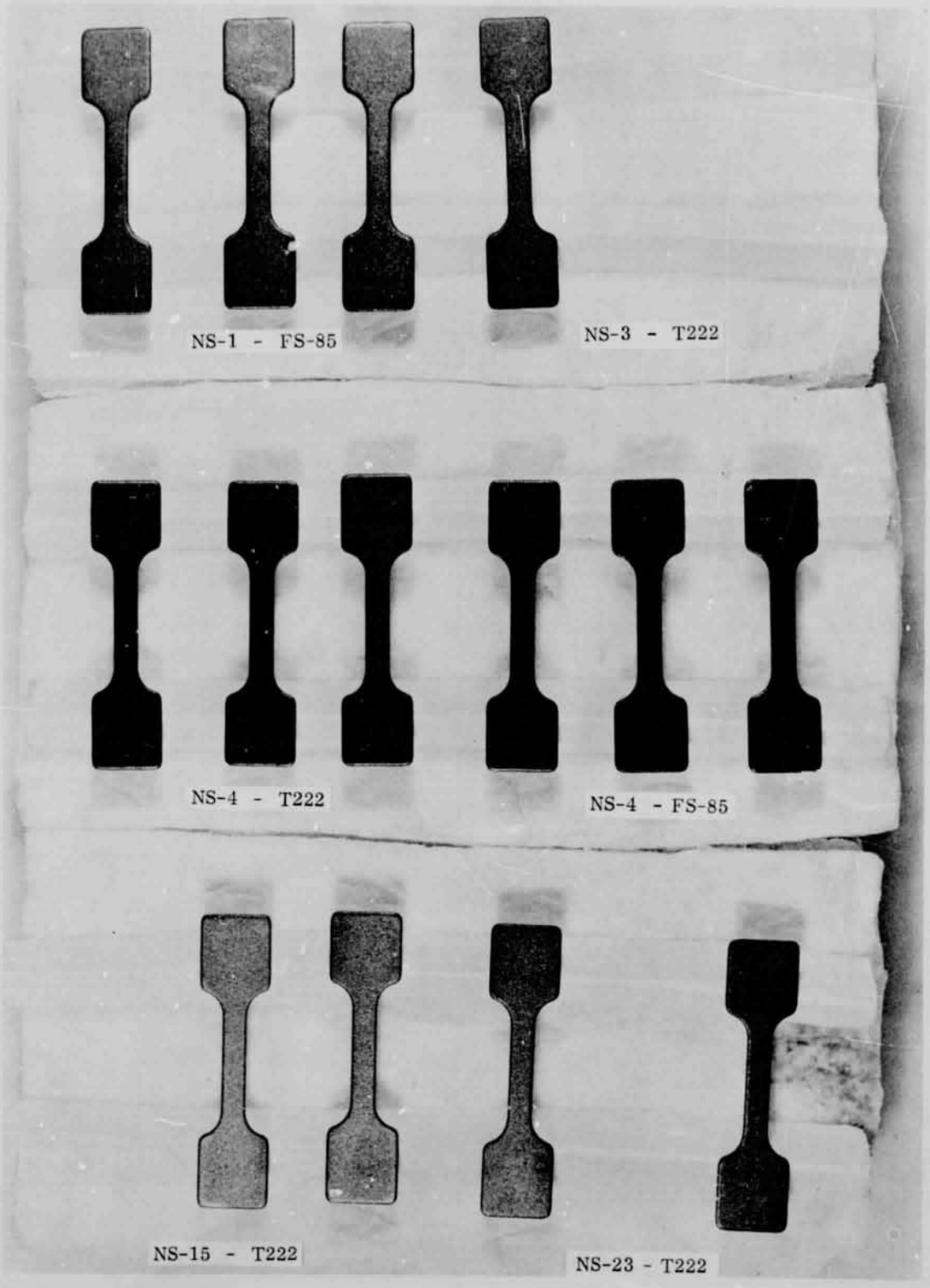


FIGURE 47. MECHANICAL TEST SPECIMENS FOLLOWING 391 HOURS OF CYCLIC OXIDATION (Failures shown by vacancies occurred after a slow furnace cool from 2400° F to 1400° F after 227 hours of testing.)

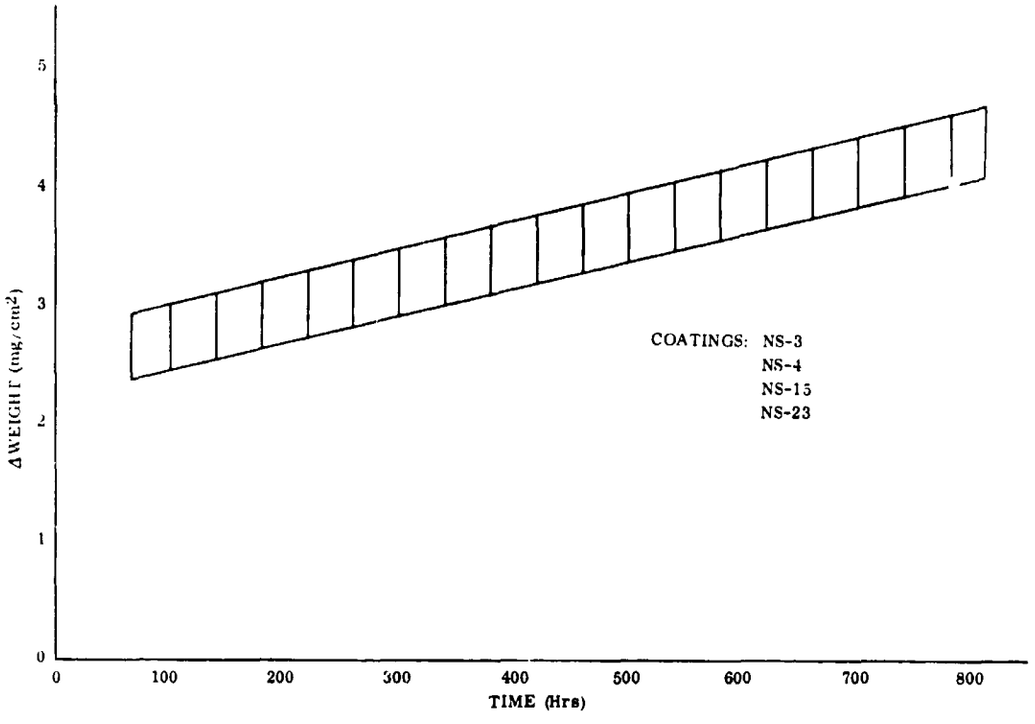


FIGURE 48. RELATION OF WEIGHT GAIN TO TIME FOR 800-HOUR, 2400° F CYCLIC OXIDATION OF COATED T222

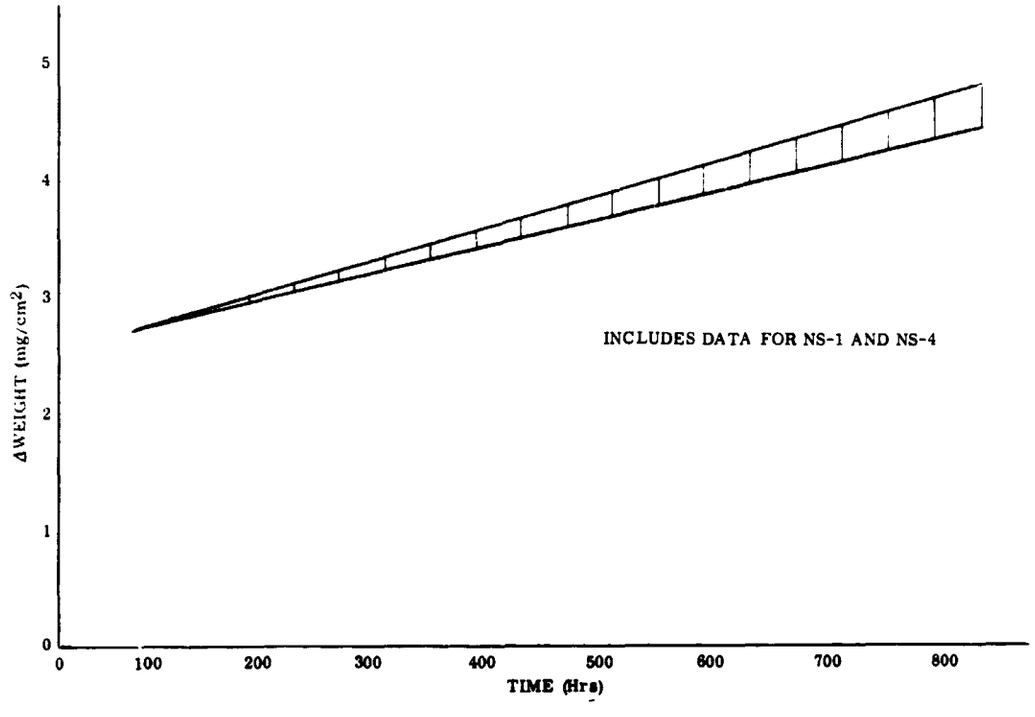


FIGURE 49. RELATION OF WEIGHT GAIN TO TIME FOR 800-HOUR, 2400° F CYCLIC OXIDATION OF COATED FS-85

The metallography of specimens after exposure to 800 hours of cyclic 2400° F oxidation varies only slightly from 200-hour oxidation covered in Section 3.3.2. Typical examples of oxidized coatings are shown in Figures 50 through 56. The major differences noted in 800 hours of oxidation as compared to 200 hours of oxidation are:

- Increased porosity in the coating
- Slight increase in the external oxide thickness
- Disappearance of the titanium-rich diffusion zone in T222 substrate beneath coatings such as NS-4
- Fewer occasions where modifier cracks are continuous through the external oxide (glass)

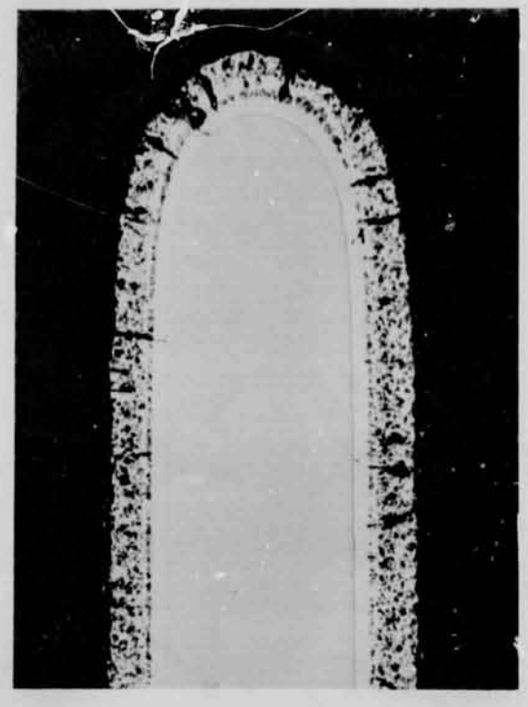
Electron microprobe analyses were conducted both before and after 800 hours of 2400° F oxidation. The results of these analyses were used to determine the compositional changes in coating and substrate as a result of oxidation. The major effort was concentrated on the evaluation of the NS-4 coating, which had performed so outstandingly in oxidation-erosion tests (Sec. 3.4.5).

An experimental uncertainty of approximately 0.0005 inch in the determination of the diffusion distances is probable as a result of variation of coating thicknesses with location on a single specimen and variation from specimen to specimen.

The results from four sets of electron microprobe analyses are tabulated adjacent to the microstructures in Figures 54, 55 and 56 (Sheets 1 and 2). The results of the analyses of NS-1 (TNV-7, Ref. 1) and NS-4 are discussed together because the compositions NS-1 (35Mo35W15Ti15V) and NS-4 (20Mo50W15Ti15V) are sufficiently similar that the diffusion data for the titanium and vanadium components should be comparable. A detail of each figure is given below.

- Figure 54. Electron Microprobe Analysis - NS-4 Coated T222 Sintered 3100° F for 15 Hours - As Silicided

  Points 1 through 5 are in the substrate, i.e., below the modifier/substrate interface. Diffusion of titanium and vanadium is indicated to approximately 0.002 inch below the interface. The maximum concentration of titanium occurs at point 3 (Ti = 1.1 percent). Only trace quantities of titanium were present in the coating, i.e., 0.2 percent maximum. The maximum vanadium concentration (V = 5.8 percent at point 6) was reached in the modifier layer near the interface and decreased to 2.9 percent



EDGE VIEW

Magnification: 40X

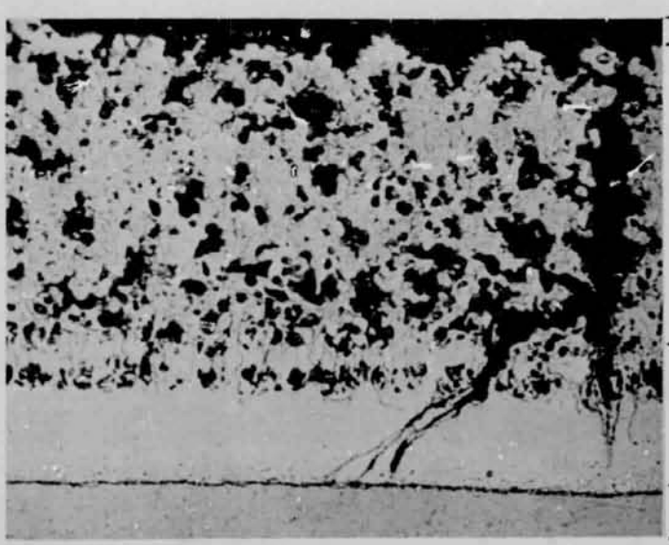
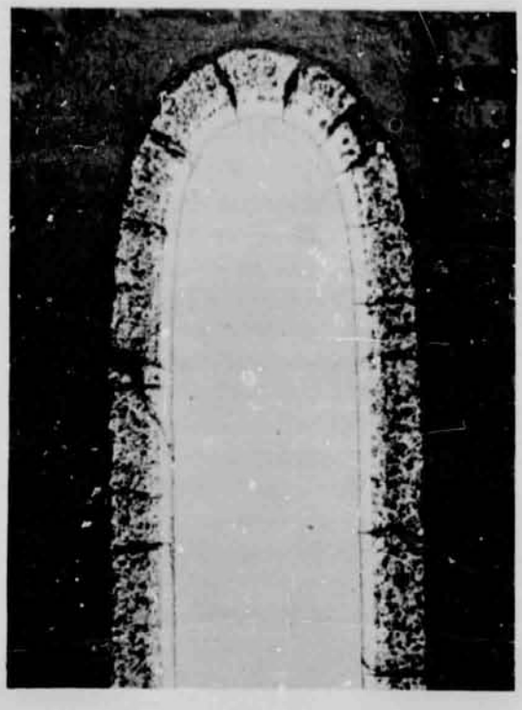


FIGURE 50. NS-3 COATED T222 AFTER 800 HOURS OF 2400°F CYCLIC OXIDATION

FIGURE 51. NS-3 COATED T222 AFTER 800 HOURS OF 2400°F CYCLIC OXIDATION



EDGE VIEW

Magnification: 40X

FLAT SECTION

Oxide

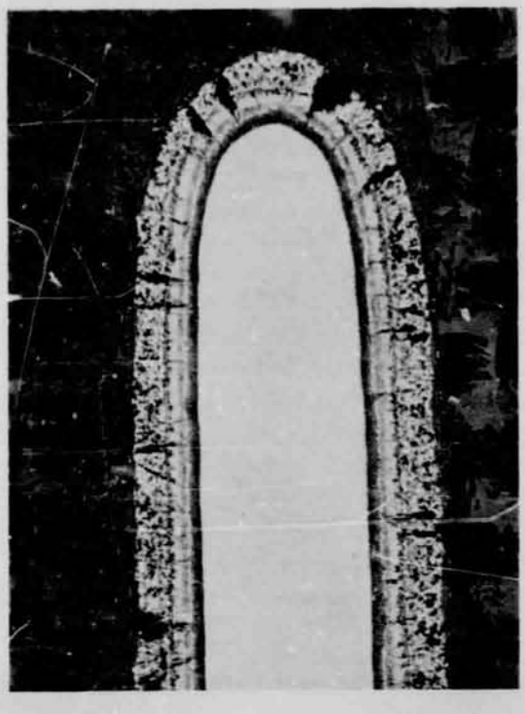
Silicided Modifier Zone

Silicide of Diffusion Zone

T222

Magnification: 250X

FIGURE 52. NS-4 COATED T222 AFTER 800 HOURS OF 2400°F CYCLIC OXIDATION



EDGE VIEW

Magnification: 40X

FLAT SECTION

Oxide

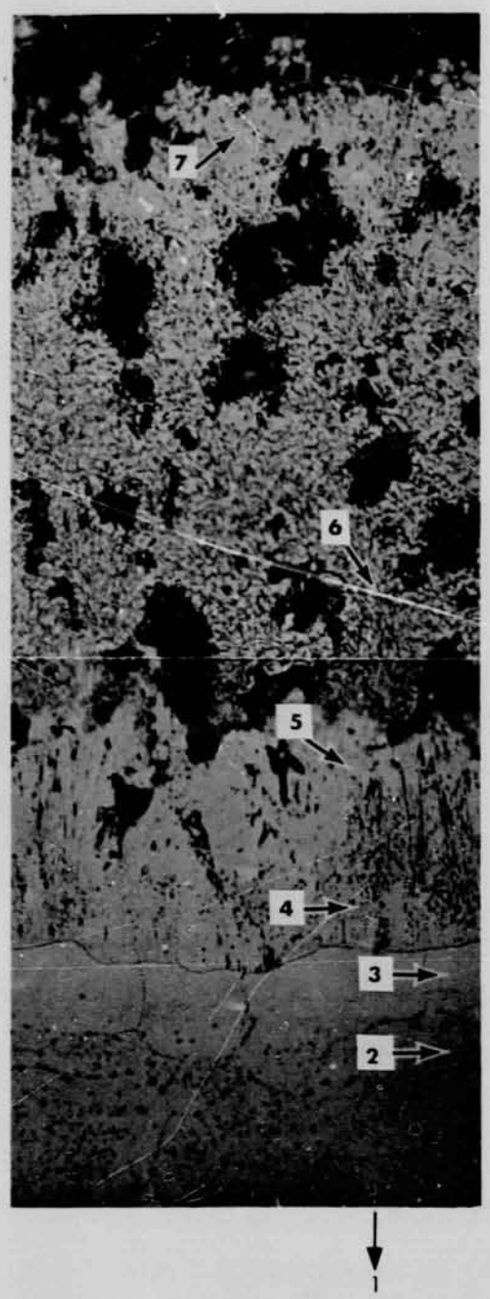
Silicided Modifier Zone

Silicide of Diffusion Zone

FS-85

Magnification: 250X

FIGURE 53. NS-4 COATED FS-85 AFTER 800 HOURS OF 2400°F OXIDATION



NS-4 Coating on T222 Alloy

Sintering Temperature: 3100°F

	Composition (Wt. %)						Silicon Modifier Atomic Ratio
	Si	Ti	V	Mo	Ta	W	
℄ 1	2.2	--	0.1	--	88.3	9.0	--
2	2.3	0.1	0.1	0.2	85.9	8.9	--
3	2.4	1.1	2.6	--	83.6	8.6	--
4	20.3	0.8	2.8	--	51.2	6.1	1.9
5	22.1	0.3	2.4	1.0	40.9	15.3	2.1
6	47.5	0.2	5.8	4.9	--	30.5	5.0
7	44.3	0.1	2.9	8.2	--	32.3	5.0

Magnification: 750X

FIGURE 54. ELECTRON MICROPROBE ANALYSIS OF NS-4 COATING (15-Hour 3100° F Vacuum Sinter Plus Pack Siliciding), AS COATED

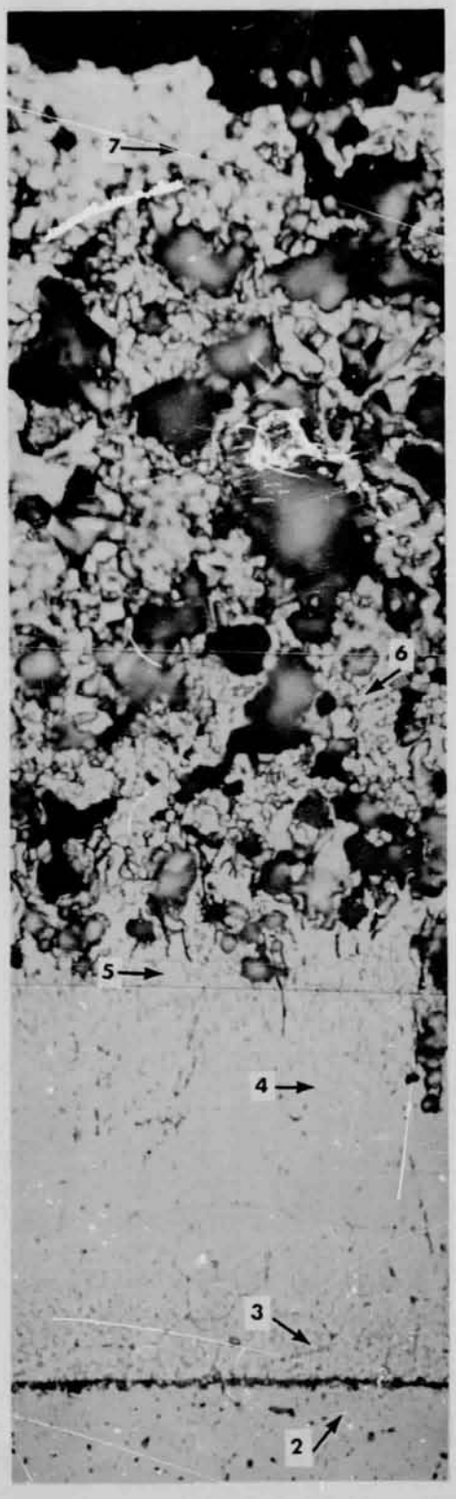
vanadium at the coating surface. The lower volatility of V probably permitted greater time for alloying, which further reduced the vapor pressure and total vaporization loss of vanadium. At point 6 there did not appear to be any loss of V when the original concentration was corrected for silicon dilution. The ratio of Mo/W at the surface, point 7, approaches that of the original modifier, indicating that no vaporization of these elements occurred. The silicon concentration in the coating gives a Si/M (silicon/metal) atomic ratio of 5 at points 6 and 7, while points 4 and 5 (substrate silicide) give Si/M ratios approaching 2. The high Si/M ratios are probably due to a high oxygen content at these points or to an error in the measurement of silicon; some excess silicon could, however, be entrapped in the coating.

- Figure 55. Electron Microprobe Analysis - NS-4 Coated T222 Sintered at 2760° F for 15 Hours - Silicided 2150° F, 16 Hours Oxidation Tested at 2400° F for 800 Hours

Points 1 through 5 are located in the original substrate, an assumption based on appearance and the concentration of tantalum, tungsten, and molybdenum. At points 3 and 4 the principal silicide appeared to be Ta_5Si_3. Points 6 and 7 appeared to be disilicides, but the analyses provides a Si/M ratio near 5, similar to the "as-fired" coating. Considerable uncertainty exists in calculating the Si/M atomic ratio because of the change in the average molecular weight of the metallic components (V, Mo, W and Ta). Further, the computer program corrections have a marked effect on the reported concentration of Si if the concentration of other elements is not exactly known. A point to note in this analysis is the almost complete absence of titanium in the coating after test. This again illustrates the difficulty of retaining this element in the vacuum sintered modifier.

- Figure 56 (Sheet 1 of 2). Electron Microprobe Analysis - NS-4 Coated FS-85 - Sintered at 2760° F for 15 Hours - Silicided 2150° F for 16 Hours

Points 1 to 4 are located in the original substrate material. Diffusion of titanium and vanadium occurred to a depth of at least 0.003 inch below the pre-sintered interface. The concentration of both elements was quite low - 2 to 3 percent for titanium and 1 to 2 percent for vanadium. Points 5 and 8 show areas that were molybdenum-rich. The data from points 5 and 8, as compared to point 7, indicated that alloying of titanium and vanadium with molybdenum is much more rapid than with tungsten. Retention of the vanadium and titanium at the level noted shows that alloying considerably reduced the activity and, consequently, the vapor pressure of these elements. The silicon concentration again appeared



NS-4 Coating on T222 Alloy

Sintering Temperature: 2760°F
Oxidation: 800 Hours at 2400°F

	Composition (Wt. %)						Silicon Modifier Atomic Ratio
	Si	Ti	V	Mo	Ta	W	
℄ 1	2.0	--	0.1	--	88.3	9.0	--
2	2.0	0.1	0.1	--	84.3	9.0	--
3	7.4	0.1	0.3	--	75.6	8.2	0.6
4	8.0	0.1	0.1	--	72.6	7.8	0.6
5	21.1	1.7	1.8	1.1	52.0	10.9	1.8
6	56.8	0.1	3.3	8.2	--	28.2	6.5
7	44.7	--	3.1	4.1	--	32.7	5.7

Magnification: 750X

FIGURE 55. ELECTRON MICROPROBE ANALYSIS OF NS-4 COATING (15-Hour 2760°F Vacuum Sinter Plus Pack Siliciding) AFTER OXIDATION TESTING AT 2400°F

NS-4 Coating on FS-85 Alloy

Sintering Temperature: 2760°F - 15 Hours
As Sintered

	Composition (Wt. %)							Silicon Modifier Atomic Ratio
	Si	Ti	V	Mo	Ta	W	Cb	
℄ 1	1.4	--	--	--	26.5	10.5	62.1	--
2	1.8	2.4	0.8	--	26.2	9.9	57.7	--
3	38.8	2.3	0.7	--	3.6	3.6	31.0	3.2
4	40.3	2.3	1.1	--	2.5	6.2	28.0	3.4
5	68.2	6.7	4.0	18.4	0.5	2.0	0.1	5.7
6	34.2	3.6	2.9	10.6	--	34.2	--	2.9
7	36.2	0.3	1.5	--	--	65.2	--	3.3
8	65.9	8.3	3.9	36.3	--	--	--	3.7

Magnification: 750X

FIGURE 56. ELECTRON MICROPROBE ANALYSIS OF NS-4 COATING (Sheet 1 of 2)

very high with the coating Si/M atomic ratio averaging greater than 3.

- Figure 56 (Sheet 2 of 2). Electron Microprobe Analysis - NS-4 Coated FS-85 - Sintered at 2760° F for 15 Hours - Silicided 2150° F for 16 Hours Oxidation Tested at 2400° F for 800 Hours

  Points 1 through 5 are located in the original substrate, and assumption based on appearance and the concentration of tantalum, tungsten, and molybdenum. At points 3, 4 and 5 the principal silicide appeared to be M_5Si_3. Points 6, 7, 8 and 9 show a broad variation in composition with silicon to modifier atomic ratio varying from 1.2 to 4.8. The results indicate that the coating is probably a mixture of M_5Si_3, MSi_2 and SiO_2. The high localized retention of titanium and vanadium at points 6 and 8 is difficult to explain since the EMP analysis on the comparable T222 coated specimen (Fig. 55) showed no comparable areas of high concentration. A possible explanation is that the beam impinged on an oxide phase through part of the counting cycle. The oxide could be expected to be relatively high in these elements in addition to silicon. High molybdenum and tungsten would not, however, be expected in the oxide during the 2400° F exposure.

  A comparison between the "as-coated" EMP results and microstructure (Fig. 56, Sheet 1 of 2) and those after 800 hours of testing at 2400° F (Fig. 56, Sheet 2 of 2) show essentially no additional penetration of silicon into the substrate as a result of this long exposure; however the total silicon content is markedly lower in the oxidized specimen. This indicates that the principal diffusing element is silicon and its diffusion direction is from the substrate silicide toward the silicided W-Mo-Ti-Si modifier and surface. It can be tentatively concluded from this observation that the diffusion rate in the modifier is higher and the free energy of formation of the modifier silicide is more negative than that of the substrate silicides.

Electron beam microprobe analyses of an iron-containing coating (NS-23, 15Mo63W15Ti5V2Fe) revealed no detectable iron in the substrate or coating after vacuum sintering at 2760° F for 15 hours.

Eight basic points were brought out by the electron beam microprobe analyses:

(1) Titanium is almost completely volatilized in the sintered coating.

(2) Molybdenum alloys more readily than tungsten with both vanadium and titanium, permitting a higher percentage retention of these elements.

NS-4 Coating on FS-85 Alloy

Sintering Temperature: 2760°F
Oxidized 800 Hours at 2400°F

	Composition (Wt. %)						Silicon Modifier Atomic Ratio
	Si	Ti	V	Mo	Ta	W	
℄ 1	0.9	--	0.1	0.2	26.5	10.5	--
2	1.0	--	0.1	0.1	26.5	9.5	--
3	9.4	--	--	--	20.9	8.2	--
4	16.1	0.7	0.3	--	15.7	5.4	--
5	22.8	2.2	3.4	--	11.7	5.1	--
6	30.6	4.5	17.2	7.3	--	34.2	1.6
7	42.6	--	1.6	14.0	--	25.9	4.8
8	25.6	4.3	18.3	11.2	--	36.4	1.2
9	27.6	0.1	1.8	10.2	--	21.7	3.8

Magnification: 750X

FIGURE 56. ELECTRON MICROPROBE ANALYSIS OF NS-4 COATING (Sheet 2 of 2)

(3) The presence of titanium does not appear to be important to the protective properties of the coatings, since it is absent from the surface layer.

(4) Vanadium, by its presence, appears to be required.

(5) The coating is non-uniform in composition, but is more uniform in the high molybdenum areas than in the high tungsten areas.

(6) Titanium and vanadium alloying with the substrate is not adequate to have a significant influence on the oxidation rate of the substrate alloy even at 1600° F (concentration of vanadium and titanium is well below the optimum for oxidation resistance and is rapidly lost from the substrate by diffusion to the surface during oxidation testing).

(7) The silicon concentration in the coating is sufficient to reach Si/M ratios of 3 to 5 in the as-silicided condition; far in excess of the stoichiometric MSi_2.

(8) The presence of iron in a coating modifier alloy contributes to sintering, as is shown in Section 3.2.4; but is lost in a 15-hour, 2760° F sinter to yield an iron-free coating.

The extent of migration of the various elements across the substrate/coating interface is summarized in Table XVIII. The concentration gradient of vanadium, titanium and silicon for each coating/substrate process condition is plotted in Figure 57.

The curves plotted in Figure 57 are approximations from the available spot analyses. The variation in the concentrations in the spot analysis for titanium is much greater than for the other elements. The inconsistencies are the result of the high volatility of titanium coupled with the high negative free energy of formation of the oxides. Oxidation and the low volatility of TiO_2 results in localized high concentrations of titanium.

The diffusion results differ between T222 and FS-85 primarily in that the movement is more rapid through the columbium-base alloy than through the tantalum-base alloy except for silicon which diffuses at about the same rate in both alloys.

3.4.3 Mechanical Property Tests

Tensile specimens of T222 and FS-85 alloy were coated with selected compositions for evaluation of mechanical properties in the coated condition both before and after 800 hours of 2400° F cyclic oxidation. The furnace oxidation is discussed in Sections 3.4.1 and 3.4.2. The mechanical property test techniques are described in

TABLE XVIII

APPROXIMATE DISTANCES OF DIFFUSION ACROSS ORIGINAL T222 COATING/SUBSTRATE INTERFACE

Oxidation Time (Hrs)	Sinter Temp. (° F)	Coating	Substrate	Diffusion Distances (0.001 Inch) (2400° F)			
				Si	Ti	V	Ta
0(1)	2760	NS-1 TNV-7	T222	1.5	1.5	1.5	0.8
0	3100	NS-4	T222	1.5	2.2	2.2	nil
800	2760	NS-4	T222	3.3	3.3	3.3	nil
0	2760	NS-4	FS-85	2.7	3.5	3.5	0.7
800	2760	NS-4	FS-85	3.0	---	---	---

Note 1. Data from Ref. 1

Section 3.4.1. The coatings applied to T222 were NS-3, NS-4, NS-15 and NS-23 while the FS-85 specimens were coated with NS-1 and NS-4. Sintering temperature for the various modifiers ranged from 2760 to 3100° F as shown in Tables XIX and XX. A complete summary of all mechanical property testing in the uncoated, as-coated and as-oxidized for 800 hours at 2400° F conditions are presented in Tables XIX and XX. The tensile test specimens are shown in Figure 58 in the as-coated and as-oxidized conditions for 800 hours at 2400° F. The coating spalled during tensile testing in the gage length on all specimens except the FS-85/NS-4 system which was sintered at 3100° F. This clearly indicated satisfactory substrate ductility for all cases other than the 3100° F sinter of FS-85.

The results of the mechanical property tests on T222 alloy in the as-coated condition showed that ductility was not adversely affected by the high-temperature sintering (even at 3100° F) during the application of the modifier. Yield and tensile strengths were reduced between 10 and 15 percent with no significant differences resulting from coating compositions or sintering temperatures. This minor reduction in strength could result from at least four factors:

(1) The long sintering time at very high temperatures, which increased the grain size from ASTM No.9 to No. 7 after a 15-hour, 3100° F sinter

(2) The diffusion of titanium and vanadium into the substrate, slightly lowering the strength of the affected surface alloy

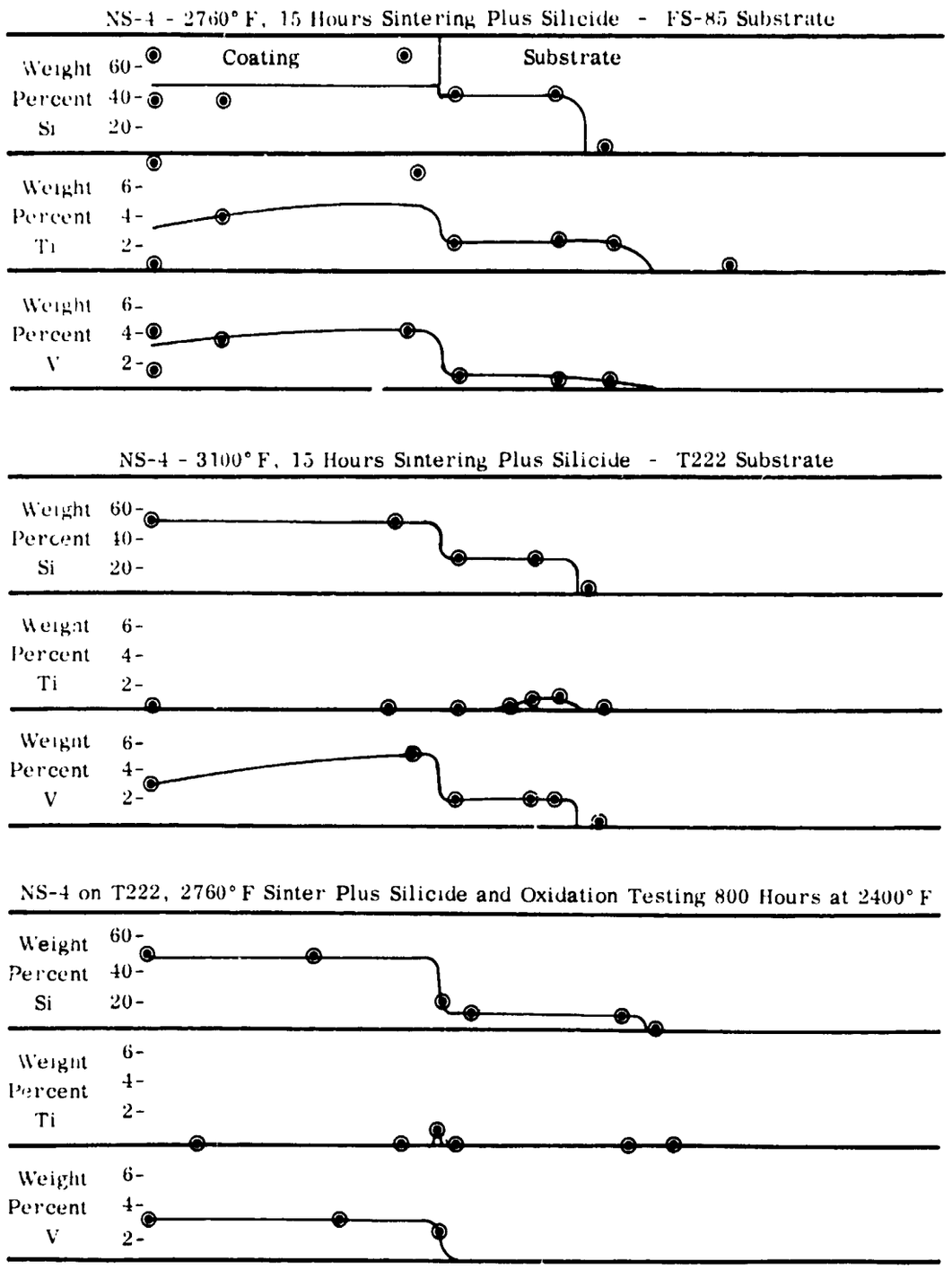


FIGURE 57. ELEMENTAL CONCENTRATIONS AS DETERMINED BY MICROPROBE ANALYSIS FOR NS-4 TESTING AT 2400° F BEFORE AND AFTER OXIDATION

TABLE XIX

TENSILE TEST RESULTS OF T222 ALLOY UNCOATED, COATED, AND OXIDIZED

Sample No.	Coating No.	Sintering Temp. (° F)	Tensile Strength x 10^{-3} lbs/in^2	Yield Strength x 10^{-3} lbs/in^2	Percent Elongation
1	None	None	118.5	89.6	21
2	None	None	116.5	104.0	22
3	None	None	116.0	102.0	21
4	None	None	111.0	104.3	23
5	None	None	116.0	102.0	23
6	None	None	115.0	104.4	22
3-1	NS-3	3100	99.3	89.5	21
3-2	NS-3	3100	100.6	92.0	18
3-3	NS-3	3100	99.7	87.0	18
4-1	NS-4	3100	98.7	87.0	16
4-2	NS-4	3100	99.0	87.0	18
4-3	NS-4	3100	96.1	84.3	15
15-4	NS-15	2760	101.5	89.5	22
15-5	NS-15	2760	101.5	93.0	23
15-6	NS-15	2760	102.8	92.3	23
23-4	NS-23	2760	98.7	92.0	10
23-5	NS-23	2760	100.1	91.0	16
23-6	NS-23	2760	101.3	77.2	20
	Coated T222 Substrates After 800-Hour 2400° F Oxidation				
3-10	NS-3	2760	89.3	78.0	17.6
4-10	NS-4	2760	105.0	95.4	6.6*
4-20	NS-4	2760	104.0	95.6	4.7*
4-30	NS-4	2760	103.0	96.0	4.0*
15-20	NS-15	2760	112.0	105.0	5.3*
15-30	NS-15	2760	111.5	100.0	4.7*
23-10	NS-23	2760	116.0	111.0	10.0*
23-30	NS-23	2760	112.0	102.5	7.3*

*Tensile specimens were machined from tested fractured bars that had undergone some previous elongation. The coating on the specimens was removed prior to machining.

TABLE XX

TENSILE TEST RESULTS OF FS-85 ALLOY UNCOATED, COATED, AND OXIDIZED

Sample No.	Coating No.	Sintering Temp. (°F)	Tensile Strength x 10^{-3} lbs/in^2	Yield Strength x 10^{-3} lbs/in^2	Percent Elongation
1	None	None	90.3	69.6	25
2	None	None	93.0	71.0	26
3	None	None	91.7	70.4	25
1-1	NS-1	940	86.0	64.0	18
1-2	NS-1	2940	86.6	64.0	21
1-3	NS-1	2940	88.0	66.4	18
4-1	NS-4	3100	41.4		.1
4-2	NS-4	3100	26.7		.1
4-3	NS-4	3100	26.7		.1
	Coated FS-85 Substrates After 800-Hour 2400° F Oxidation				
1-10	NS-1	2760	64.7	53.0	21
1-20	NS-1	2760	65.1	54.0	20
1-30	NS-1	2760	66.7	56.6	22
4-10	NS-4	2760	67.7	57.0	17
4-20	NS-4	2760	70.7	57.0	14
4-30	NS-4	2760	70.1	58.0	14

(3) The notches in the coating as a result of differential expansion cracking of the silicide

(4) Silicon penetration (up to 0.002 inch) into the substrate

After exposure for 800 hours at 2400° F, the coated T222 alloy specimens showed only slight additional loss in either yield or tensile strength, shown graphically in Figure 59. The remaining NS-3 specimen showed an additional 10 percent loss in both ultimate and yield strength, which was the greatest loss for the group.

The cross-sectional area used for the evaluation of all specimens was that of the specimens prior to coating. In the initial mechanical property tests of the large specimens, it was observed that several specimens failed in a grip end. Investigation of the possible causes revealed that the use of sodium hydroxide for stripping the

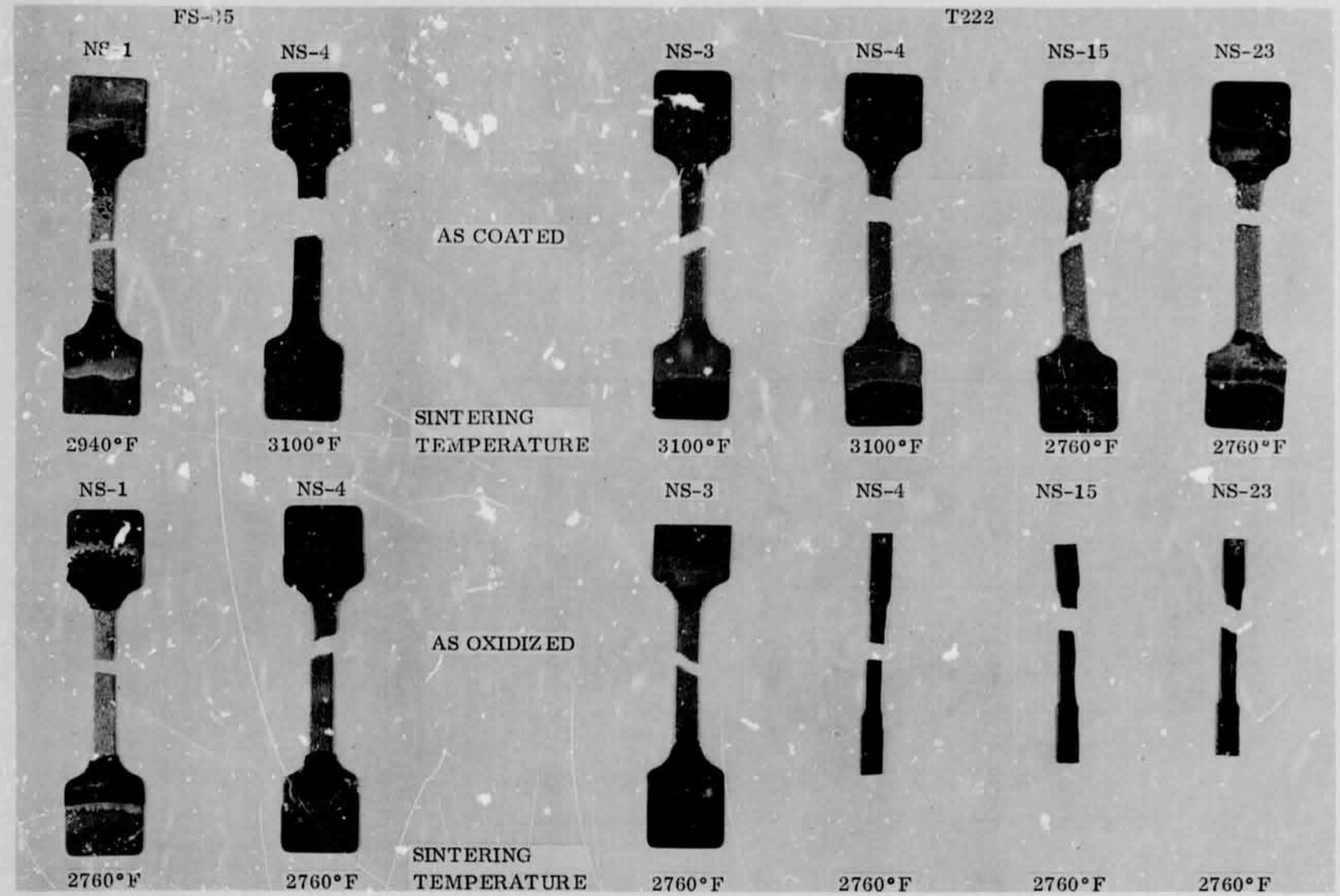


FIGURE 58. TESTED TENSILE SPECIMENS OF T222 AND FS-85 AS-COATED AND AS-OXIDIZED FOR 800 HOURS AT 2400°F

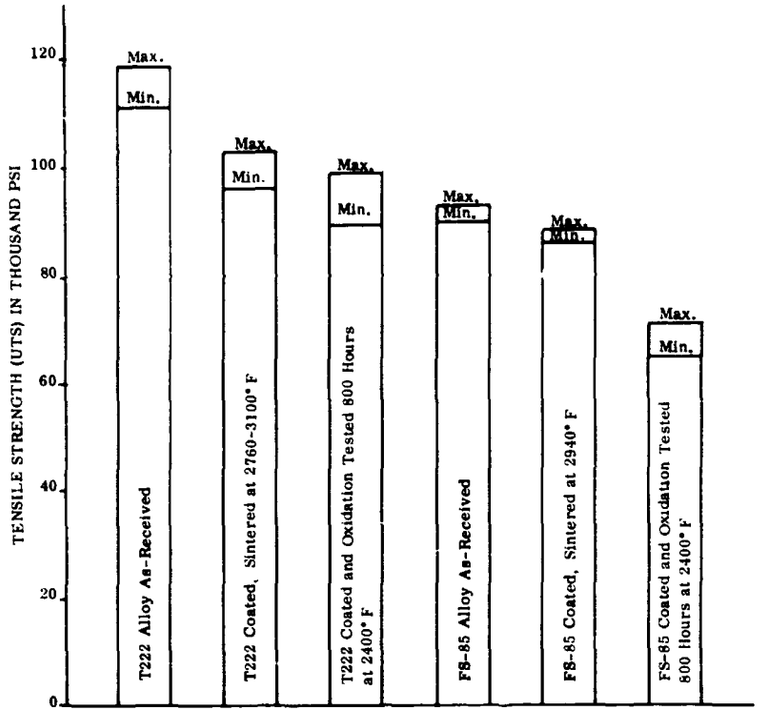


FIGURE 59. ROOM TEMPERATURE TENSILE STRENGTH OF T222 AND FS-85 IN THE AS-RECEIVED, AS-COATED, AND AS-OXIDIZED CONDITIONS (Cross-Sectional Area Used for Calculations was Original Area Prior to Coating)

silicide from the ends (to facilitate gripping) had caused hydrogen or oxygen embrittlement. Thus, in order to obtain an indication of the mechanical property data, new miniature test bars were machined from the standard specimens as shown in Figure 60. These miniature test specimens were used in obtaining most of the data on the oxidized T222 alloy.

Unfortunately, the elongation values on the 800-hour exposed specimens are less than the true value since the tests were not performed on standard specimens but rather on miniature specimens machined from the originally tested standard bars. With the reduced sections of these miniature specimens, the values become less representative. In addition, these specimens had undergone some prior elongation when the standard bars were tested.

Mechanical property test data for coated FS-85 brought out one very significant point. A sintering temperature of 3100° F is too high for this alloy. The mechanical property test results of NS-4 coated FS-85 showed greater than a 50 percent drop in

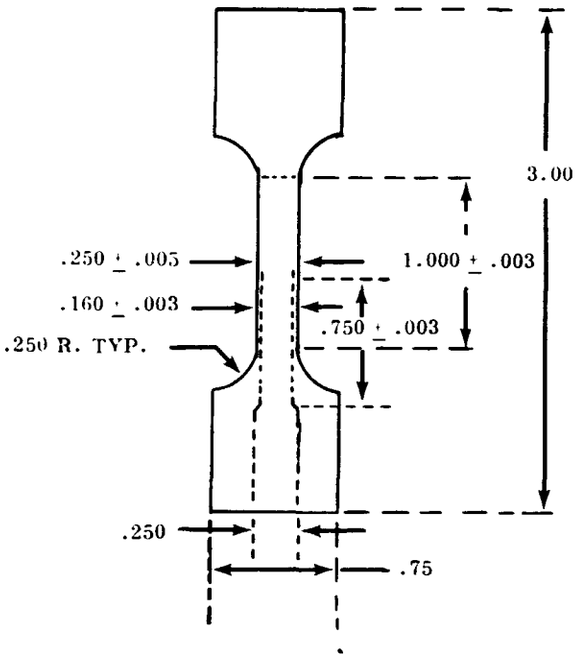


FIGURE 60. STANDARD TENSILE TEST SPECIMEN AND REDUCED SIZE TENSILE TEST SPECIMEN

ultimate tensile strength and no measurable elongation. ASTM grain size had also increased from the as-received value of No. 6 to No. 0 after 16 hours at 3100° F.

Sintering at 2940° F, however, did not strongly affect the FS-85 alloy. The reduction in tensile strength was approximately 5 percent and the reduction in yield strength was less than 10 percent. Considerable elongation - approximately 20 percent - was retained by the alloy. There was a further reduction in both the yield and tensile strengths after 800 hours of oxidation exposure. Compared to the uncoated alloy in the as-received condition, the coated specimens after exposure retained approximately 75 percent of both yield and tensile strength. The alloy retained considerable elongation.

3.4.4 Slow Thermal Cycling of Coatings on T222

To evaluate the suspected tendency toward coating failure at low temperatures, five chemistries were applied to T222 alloy test specimens.

The modifier coatings were applied using the standard application methods. The modifiers were sintered in 10^{-5} to 10^{-6} Torr vacuum for 15 hours at the following temperatures:

Coating Number	Sintering Temperature
NS-1	2940° F
NS-3	3100° F
NS-4	3100° F
NS-15	2760° F
NS-23	2760° F

These pack silicided specimens were evaluated by the test procedure described in Section 3.4.1.

All of the tested specimens are shown in Figure 61. Each specimen completed 22 cycles. The two NS-1 and the one NS-15 coated specimens failed, while NS-3, NS-4 and NS-23 survived. General factors observed were:

- The specimens showed non-uniformities in the coatings where the specimens rested on tungsten blocks for modifier sintering. At these points, the coatings were more glassy, showing the probable effect of inhibited titanium and vanadium volatilization during sintering and some possibility of modifier sintering to the rods. Failures tended to initiate at these contact points.

- The NS-1 coating developed a single pinhole on the first specimen near the end of the 22 cycles and apparently three edge defects on the second specimen, resulting in oxidation loss of a significant portion of the second sample.

- The NS-15 coating developed a single hole in the central region indicating a pinhole failure near the end of the 22 cycles.

- In all cases a yellow powder and clear, acicular crystals collected at either end of the specimen in the low-temperature zone. This condensate, analyzed by X-ray diffraction and emission spectroscopy, was found to be predominantly WO_3.

While this test does not closely simulate overall turbine conditions, it does generate coating damage similar to that observed in cooler portions of erosion bars (near the shank) and emphasizes the need for both improved modifier application and sintering techniques and modifier compositions less sensitive to slow-cycle or low-temperature failure.

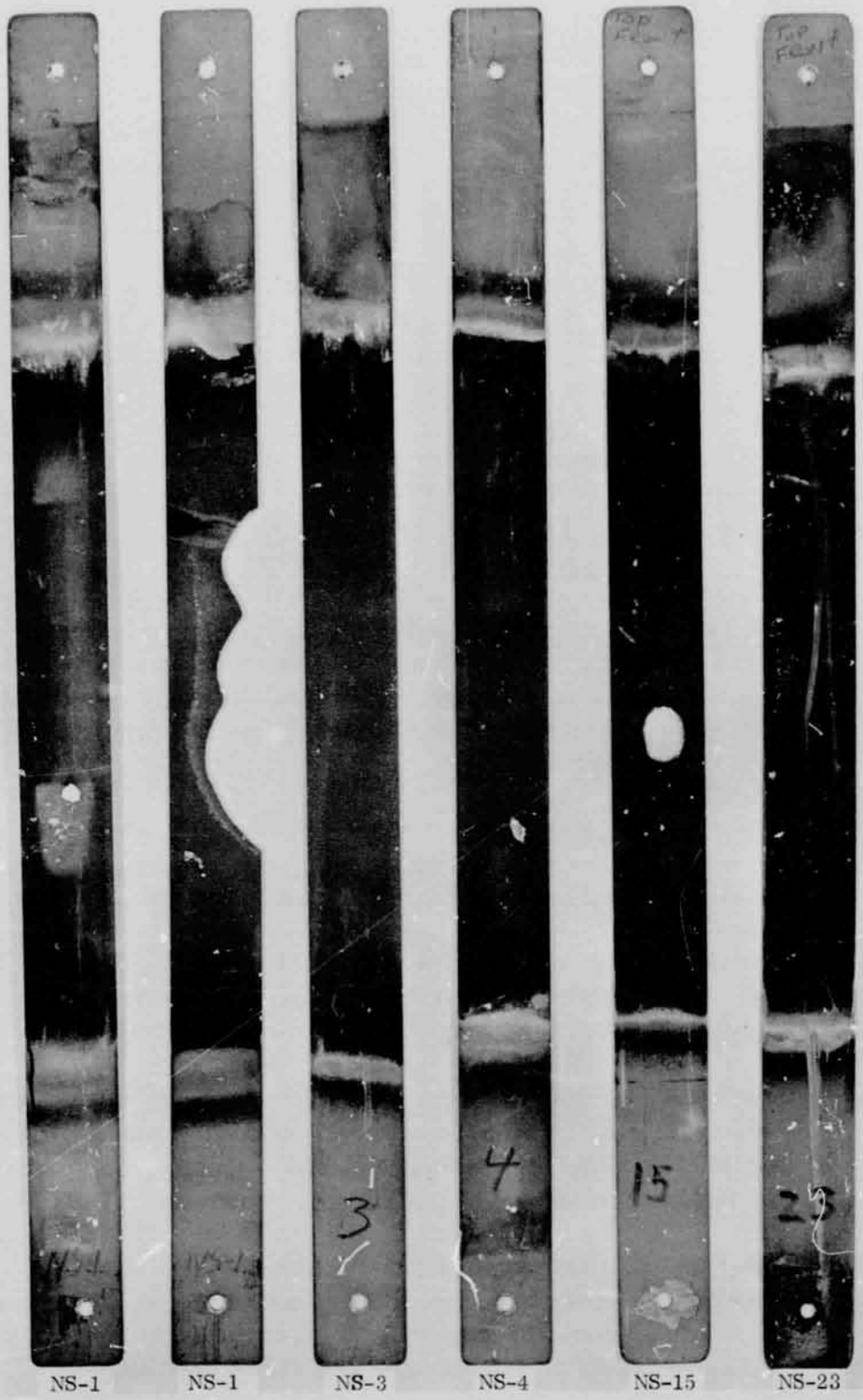


FIGURE 61. SLOW THERMOCYCLE TEST SPECIMENS AFTER 22 ONE-HOUR CYCLES FROM 850 TO 2300° F

3.4.5 Erosion Bar Test Results

Figure 62 will clarify the terminology used in this section.

In the 2400° F erosion testing, the majority of the coatings performed exceptionally well. The most outstanding of the 18 coatings tested on T222 was the silicide formed following a 15-hour, 3100° F vacuum sinter of the NS-4 modifier. The low-titanium content coating (NS-4, 3100° F sinter) shown in Figures 63, 64 and 65 developed a black vitreous coating with significantly less visible craze cracking than was observed with high titanium (NS-4, 2760° F sinter), Figure 66. These two initial low-titanium specimens survived 207 and 221 one-hour cycles and did not fail in the hot region, but on the cooler root radius. Of the four coatings tested on FS-85 alloy, NS-4 survived 186 and 164 hours and was not significantly better than NS-1, which survived 153 and 231 hours with shank and radius failure predominating rather than hot zone blade failure.

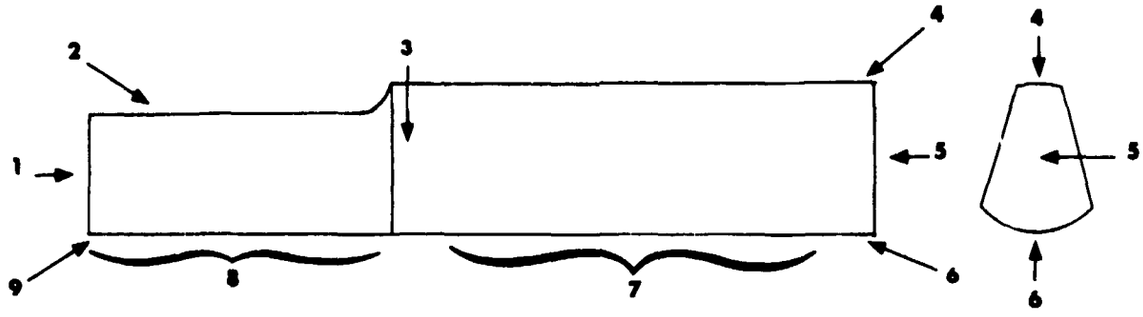
The major source of failure within the first 100 hours of test for any coating was mechanical damage. The specimens were subjected to severe mechanical and thermal stress throughout the test. The temperature gradient from the center of the wedge to the center of the shank was 800° F (wedge 2400° F, shank 1600° F). This gradient of 800° F in less than one inch can generate a high shear stress between coating and substrate and a moderate tensile stress in the coating, which in the 1600° F range may, in part, be responsible for coating failure in the shank and transition zone areas. Mechanical stresses induced by the locking bolts used to hold the bars in place in the holder, the centrifugal force generated by holder rotation, and the vibration induced by the thrust from the burner blast all compounded the stress problem substantially.

The results of the tests are summarized in bar graphs, Figures 67 and 68 and Table XXI. The time to failure has been noted as nearly as possible for each bar.

Each failure occurred up to $^{+0}_{-20}$ hours of the time designated as "failure". Specimens with shank failures were returned to test in an effort to obtain enough time on the wedges to evaluate the performance if the shank problem were corrected.

Due to severe stresses on the shanks, numerous remedial steps were taken in an attempt to alleviate the problem:

- The shanks were wrapped with glass tape to provide cushioning
- Fiberfrax was placed in the bottom of each specimen holder hole to prevent damage to the base during sample installation.



1 Base
2 Flats
3 Transitional (Radius)
4 Leading Edge
5 Tip
6 Trailing Edge
7 Wedge (Blade)
8 Shank
9 Heel

FIGURE 62. SCHEMATIC OF TYPICAL EROSION BAR WITH NOMENCLATURE OF PARTS

- A metal shim was placed over each flat to distribute the load of the locking bolt.
- Great care was taken in installing the specimens in the holder.

These precautions prevented much base and shank flat area damage, but did not eliminate shank failures.

Types of Failures

The areas of failure in oxidation-erosion rig testing are generally categorized into tip (T), blade (wedge) (B), radius (R) (transitional zone), and shank (S) failures. A typical example of each failure type is shown in Figures 69, 70, 71 and 72, respectively.

Shank Failure

The predominant testing problem, shank failure, is shown in situ in Figures 73 and 74. In the example shown in Figure 73, it is not apparent whether this is a shank or radius failure. Samples in the same group with less damage, Figure 74 (Specimen 4-1), indicate that the failure was initiated in the shank. Significantly, the condition of the coating on the blade and radius is excellent except where undercut by failure within the holder.

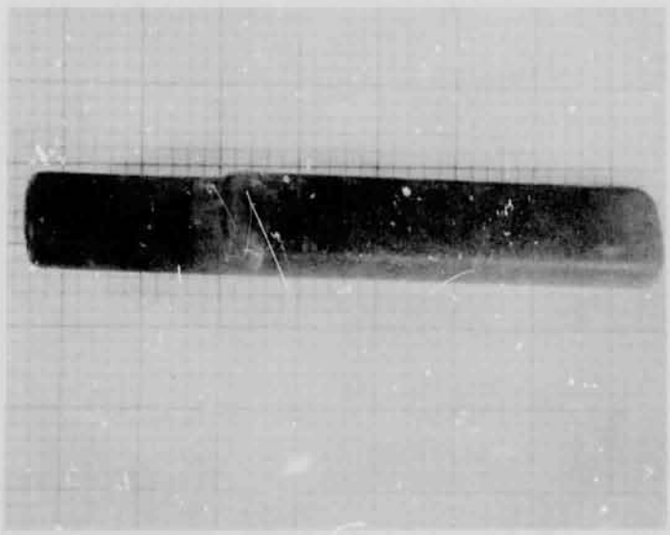


FIGURE 63. NS-4 COATED T222 EROSION BAR (MODIFIER COATING SINTERED AT 3100°F). Specimen Tested 100 Hours in 2400°F Oxidation/ Erosion.

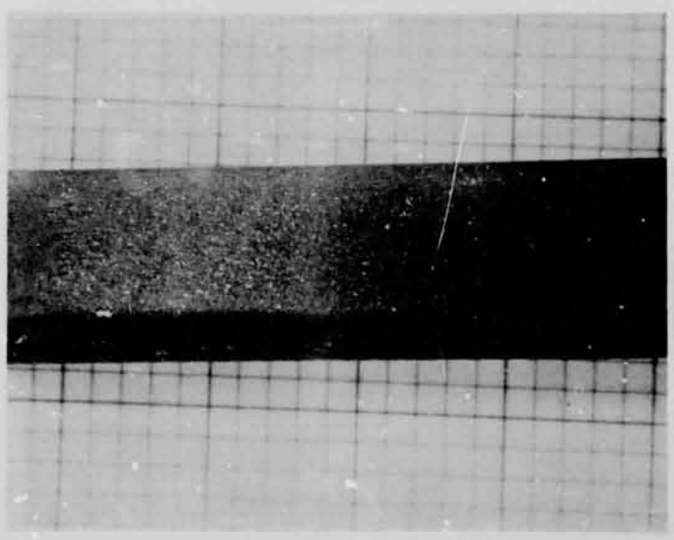


FIGURE 64. NS-4 COATED T222 EROSION BAR BLADE (MODIFIER COATING SINTERED AT 3100°F). Specimen Tested 221 Hours to Shank Failure in 2400°F Oxidation/Erosion.

FIGURE 65. NS-4 COATED T222 EROSION BAR TIP (MODIFIER COATING SINTERED AT 3100°F) AFTER OXIDATION/EROSION TESTING 32 HOURS AT 2400°F

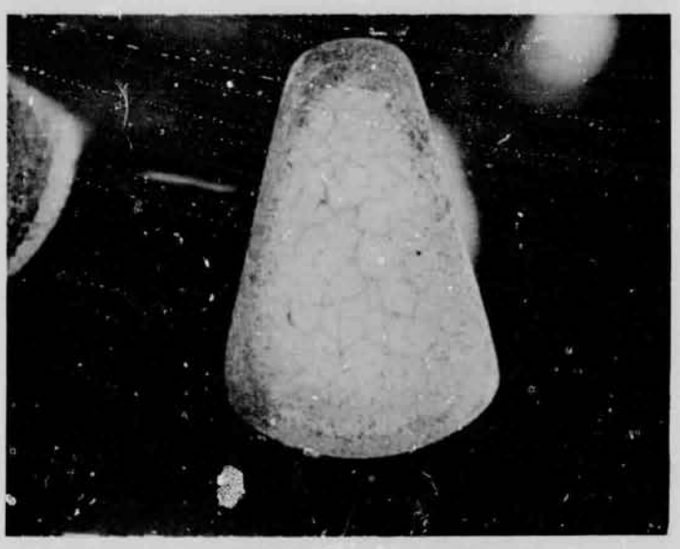


FIGURE 66. NS-4 COATED T222 EROSION BAR TIP (MODIFIER COATING SINTERED AT 2760°F) AFTER OXIDATION/EROSION TESTING 32 HOURS AT 2400°F

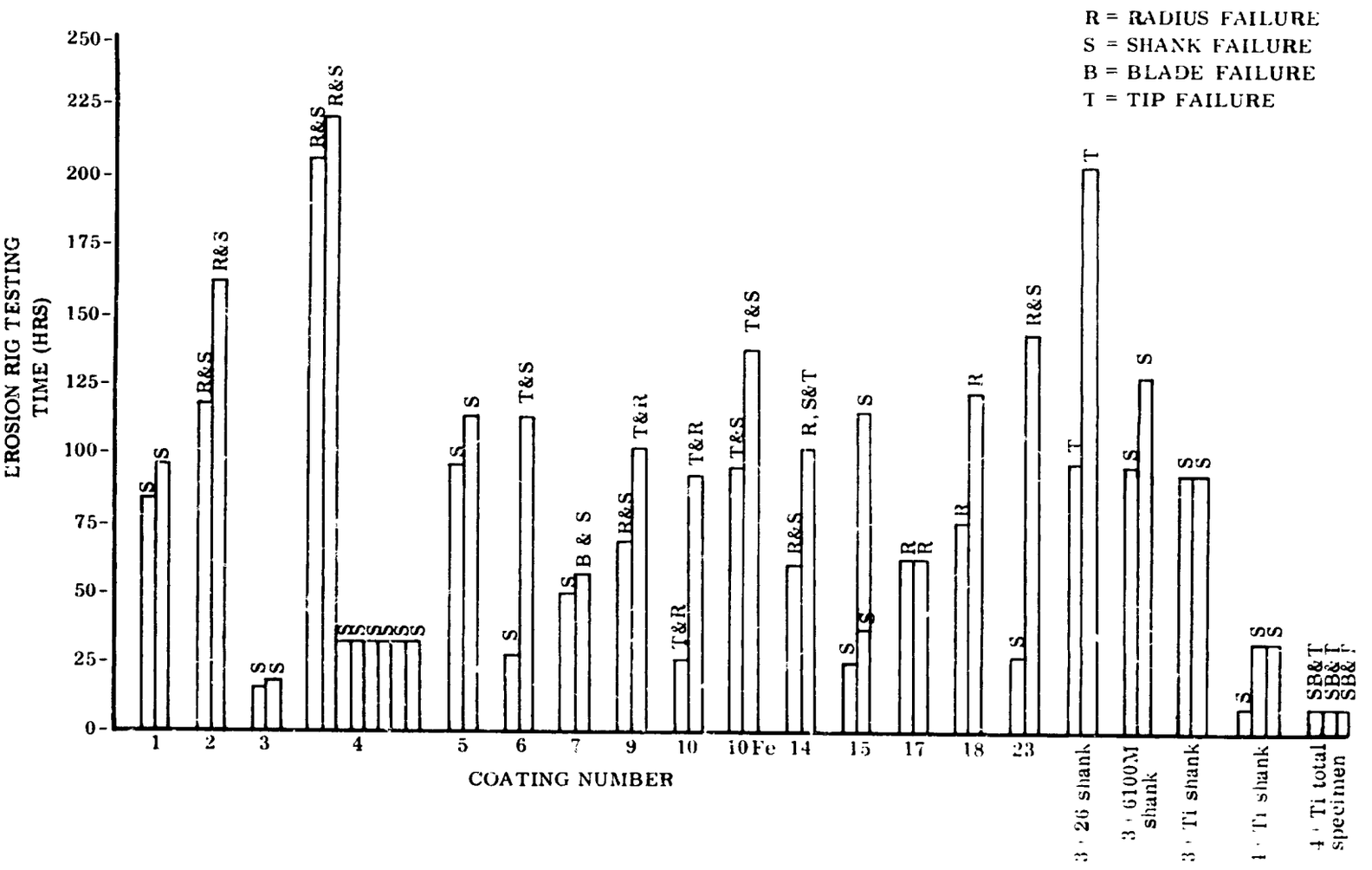


FIGURE 67. OXIDATION/EROSION RIG TEST RESULTS AT 2400°F ON T222 ALLOY

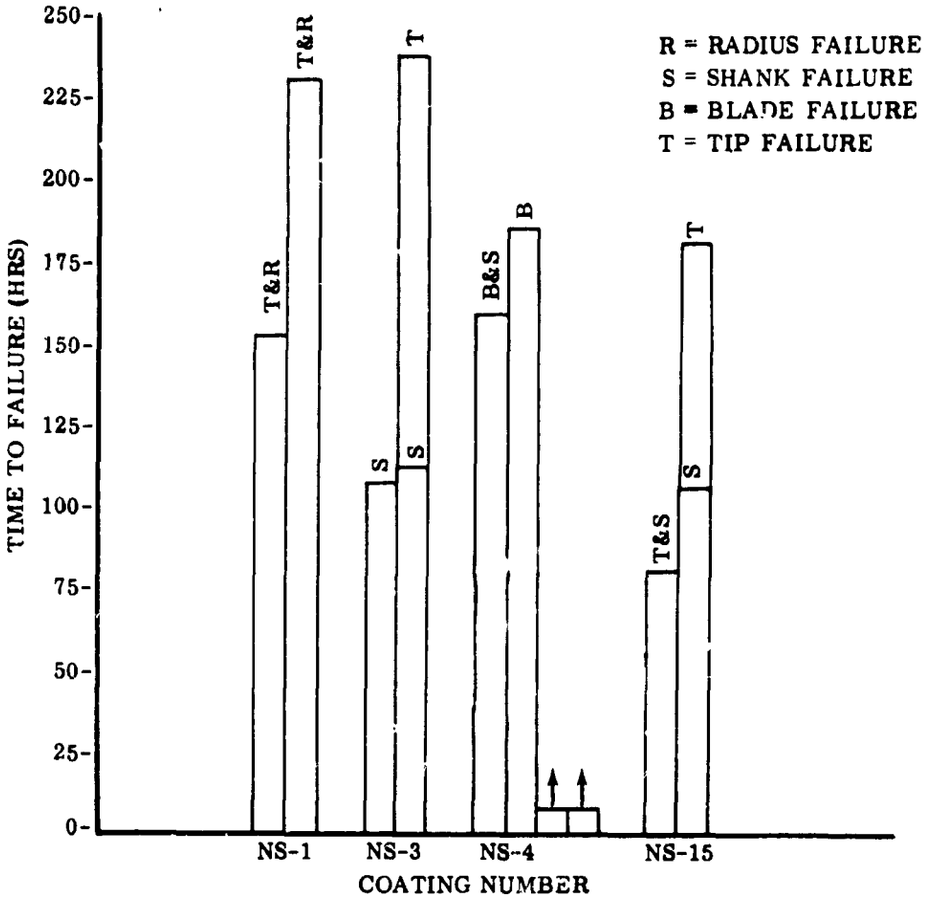


FIGURE 68. OXIDATION/EROSION RIG TEST RESULTS AT 2400° F ON FS-85 ALLOY

Two additional examples of shank damage are shown in Figures 75 and 76. Figure 75 is a typical shank failure comparable to sample 4-1 in Figure 74. Figure 76 is a specimen which has been tested for eight hours without oxidation failure. The fractures in the coating (Fig. 76) appear to be compressional shear fractures on either side of the shank, 90 degrees from the flat. The fractures support the theory that the specimen was vibrating on an axis from the lock bolt to the opposite edge of the holder. Such vibration would produce fractures 45 degrees from the axis. These fractures would eventually result in dislodged coating.

Because of the superior shank performance of coatings high in vanadium plus titanium, one of the methods evaluated to increase shank life was to fused salt plate the shank with titanium and apply the coating over the intermediate layer. Some coatings were improved, but the results were inconsistent. An example of an unsatisfactory product of this effort is shown in Figure 77. The titanium layer between the

TABLE XXI

TEST RESULTS FOR 2400° F EROSION RIG TESTS

Coating	Sample Number	Substrate	Sintering Temperature (°F)	Time to Failure	(See Fig. 62) Failure Area	Wedge Condition
NS-1	1	T222	2940	96	1, 2	Glassy, but good
	2			83	1, 2, 7	Glassy, but good
NS-2	3	T222	2940	118	1, 2, slight 3	Good
	4			162	Front 3	Good
NS-3	5	T222	3100	15	Shank total	Good
	6			18	Shank total	Good
NS-4	7	T222	3100	207	Front 3	Good
	8			[illegible]	Front 3	Good
NS-5	9	T222	2760	95	Shank total	Good
	10			113	Shank total	Good
NS-6	11	T222	2760	27		Some craze cracking (cc)
	12			113	7, 5, 6	Some cc
NS-7	13	T222	2760	56	1, 2	Wedge failure cc
	14			49	1, 2	Wedge failure cc
NS-9	15	T222	2760	68	3, 5	cc
	16			102	1, 3	cc
NS-10	17	T222	2760	25	1, 5, slight 3	cc tip
	18			92	1, 2, 3, 7	cc tip
NS-10Fe	19	T222	2760	137	2, 3, 6	cc tip
	20			94	1 5	cc tip
NS-14	21	T222	2760	[illegible]	1, 2, 3	cc tip
	22			64	1, 2, 3	cc tip
NS-15	23	T222	2760	37	Total shank	cc tip
	24			24	Total shank	cc tip
NS-17	25	T222	2760	64	[illegible]	Good
	26			64	Severe 3	Good
NS-18	27	T222	2760	121	Front 3	Good
	28			74	Front 3	Good
NS-23	29	T222	2760	26	1, slight 2	Good, cc tip
	30			142	3, slight 2	Rough, but good
NS-26 + 3	31	T222	2760	95	Front 3, 5	Good
	32			203	3, 5	Good
NS-3 + 86100M	33	T222	2760	94	Slight 1, 7	Good
	34			127	7 area	Good
Ti + NS-3	35	T222	2760	92	7	Good
	36			92	None	Good
NS-1	101	FS-85	2940	231	5	Good
	102			153	3, 5, 6	Good
NS-3	103	FS-85	3100	106	1, 2, 7, slight 3	Good
	104			113	1, 2, 7	
NS-4	105	FS-85	3100	166	6, slight 3	Good
	106			164	6, slight 3, [illegible]	Good
NS-15	107	FS-85	2760	82	3, slight 5	Good
	108			107	3, slight 5	Good

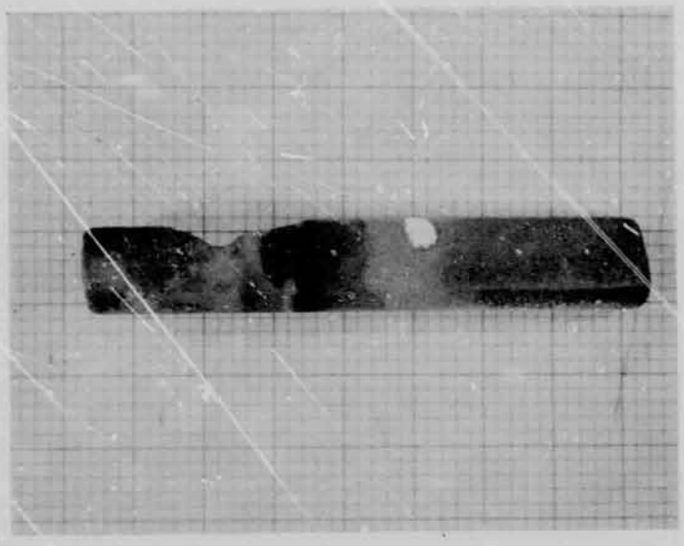


FIGURE 69. COATING NS-7 ON T222 BAR. 49 HOURS TO FAILURE - BLADE AND SHANK.

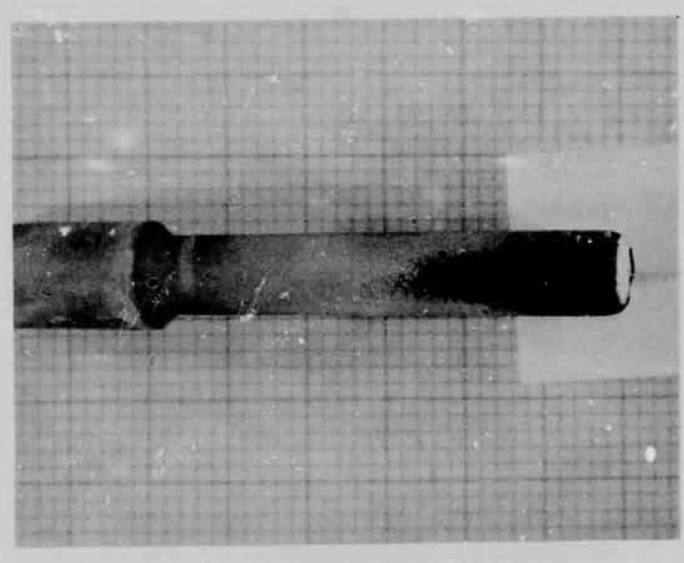


FIGURE 70. COATING NS-9 ON T222 BAR. 68 HOURS TO FAILURE - BLADE TIP.

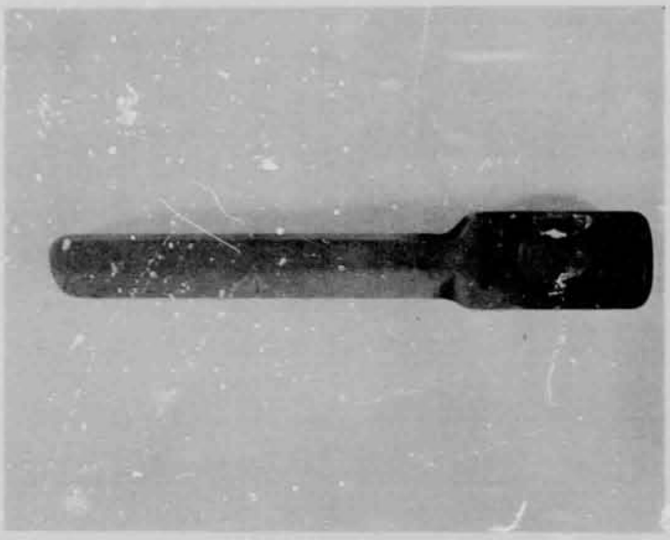


FIGURE 71. SHANK FAILURE ADJACENT TO LOCKING BOLT CONTACT POINT. Sample No. 5 (T222 Coated with NS-3).

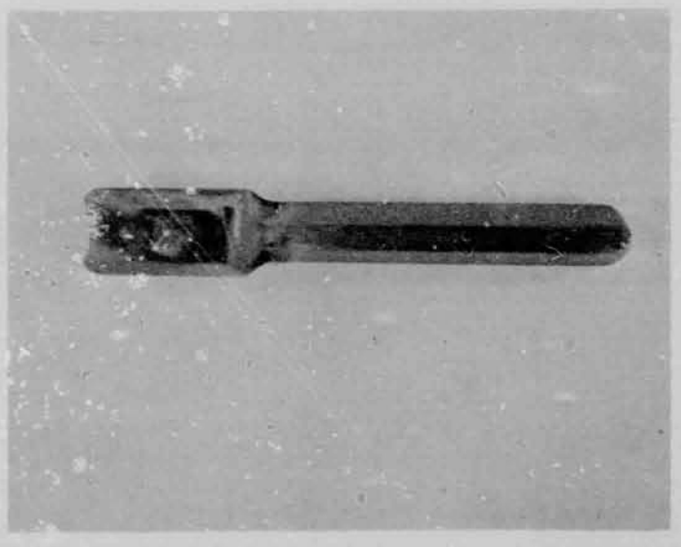
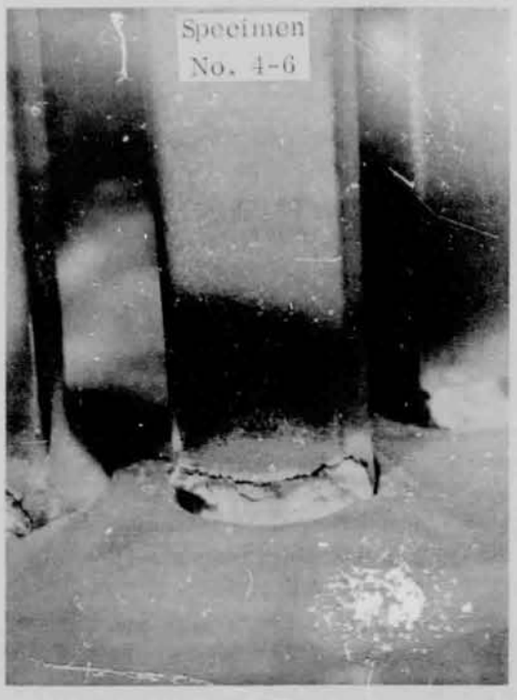


FIGURE 72. SHANK FAILURE AT BASE. Sample No. 23 (T222 Coated with NS-15).

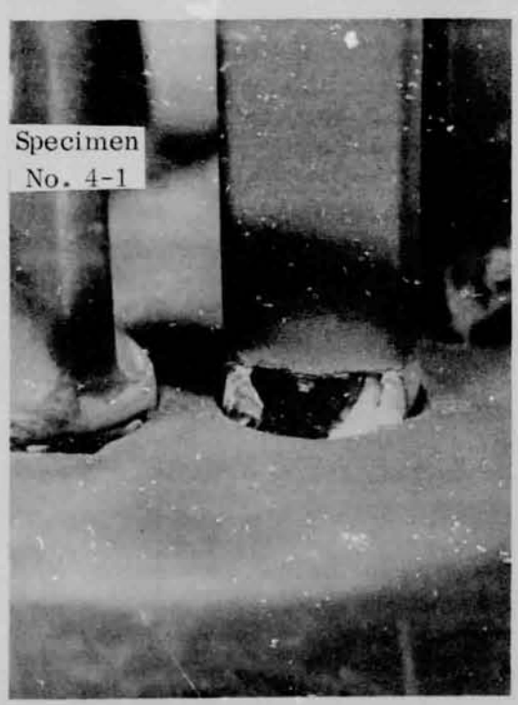


Specimen No. 4-6

Coating NS-4 (2760°F sinter)
on T222

Magnification: 2X

FIGURE 73. OXIDATION/EROSION TEST SPECIMENS IN HOLDER AFTER 32-HOUR FAILURE



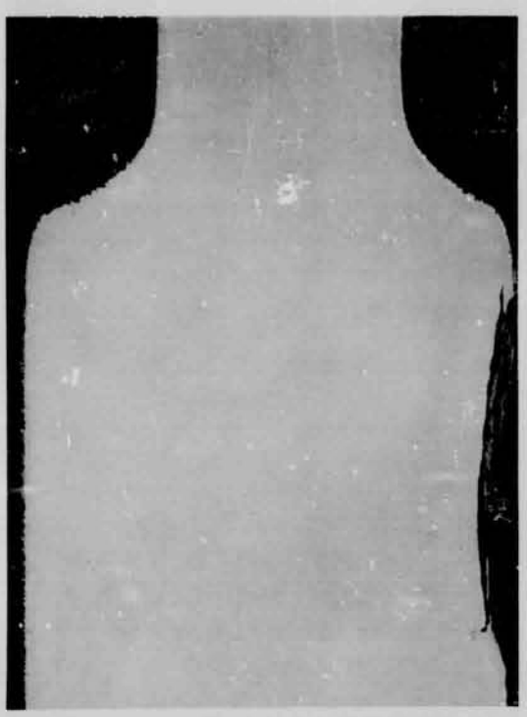
Specimen No. 4-1

Coating NS-4 (2760°F sinter) Center

Coating NS-4 (3100°F sinter) Left

Magnification: 2X

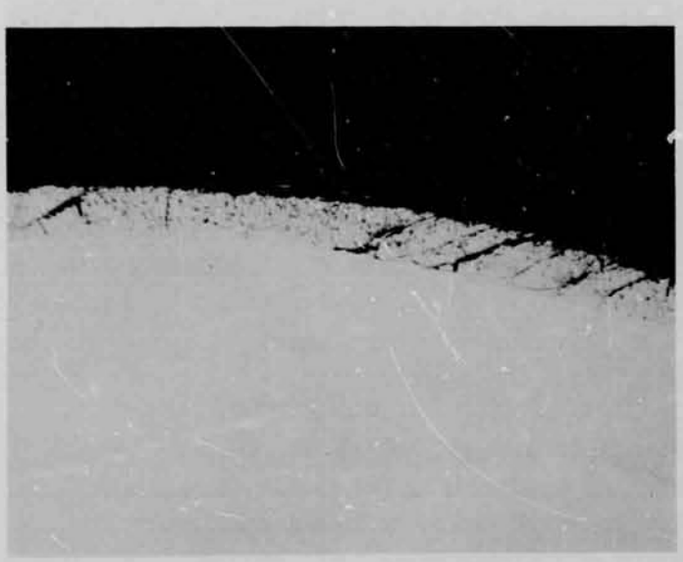
FIGURE 74. OXIDATION/EROSION TEST SPECIMENS IN HOLDER AFTER 32-HOUR FAILURE



Unetched

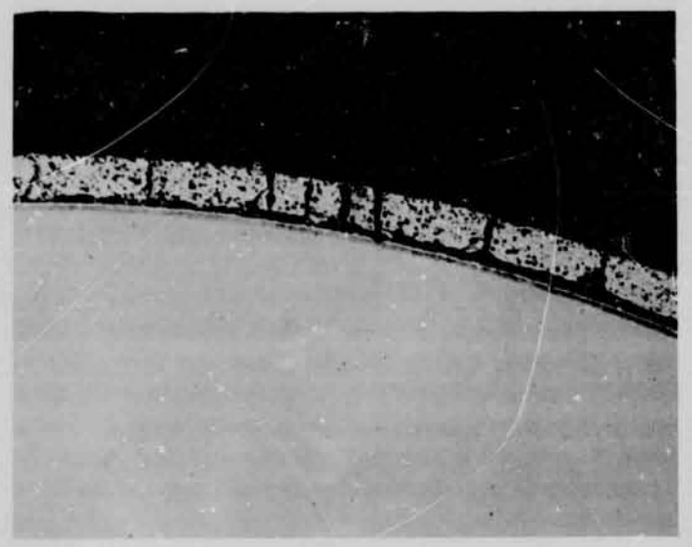
Magnification: 6X

FIGURE 75. COATING NS-4 (3100° F SINTER) ON T222 AFTER 32-HOUR SHANK FAILURE



Magnification: 40X

FIGURE 76. COATING NS-4 ON T222 AFTER 8 HOURS TEST - NO FAILURE. MECHANICALLY DAMAGED SHANK.



Magnification: 40X

FIGURE 77. T222 SUBSTRATE - 0.001 INCH TITANIUM PLATE NS-4 COATING - S6100M GLASS OVERLAY. (Voids after 8 hours testing apparently Ti vaporization from interface or Kirkendall diffusion.)

coating and substrate primarily vaporized and diffused away during sintering affording very poor bond of the modifier to the substrate. An additional attempt to provide shank protection was to overlay the coating with S6100M ceramic coating (commercially available from Solar). The ceramic coating was expected to improve low-temperature oxidation and provide some lubrication for the oscillating erosion bar root. No improvement in time to failure was noted.

An attempt was also made to temporarily repair damaged shanks by overlaying with S6100M. This was accomplished by lightly sandblasting the shank, siliciding and coating with S6100M, as shown in Figure 78. All specimens reprocessed in this manner failed in eight hours. The shank failure problem remains to be resolved before silicide coatings could be used for engine hardware.

Radius Failures

Radius failures were seldom definitely distinguishable. In most cases there was a question of whether it was shank failure undercutting the radius or radius failure extending into the shank. Two distinct examples of radius failure are shown in Figures 79 and 80.

The incipient failure shown in Figure 79 is the result of non-uniform coating application. The excessive thickness of the substrate silicide visible under the thin radius coating is evidence that the modifier was thin prior to the siliciding operation.

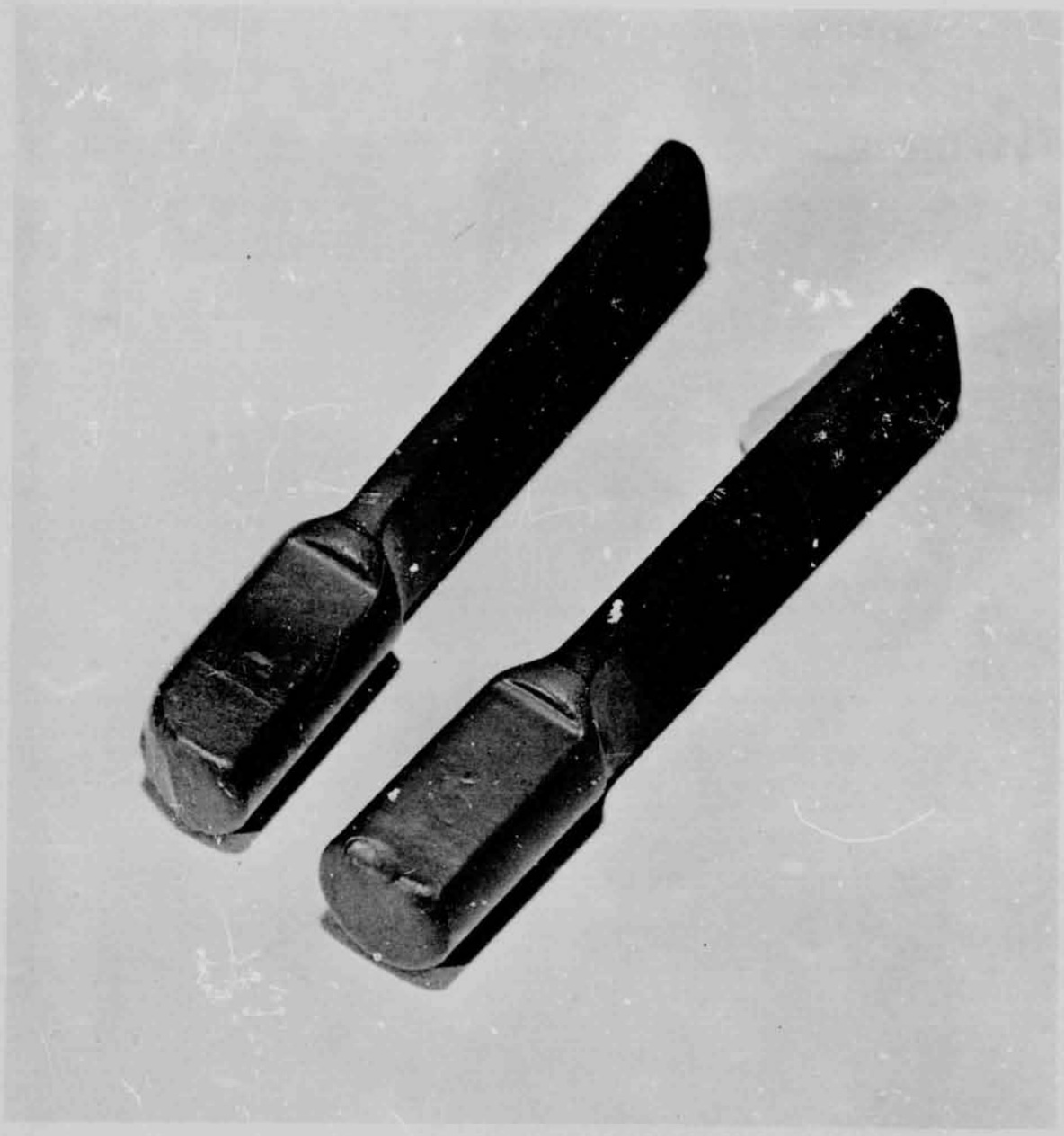
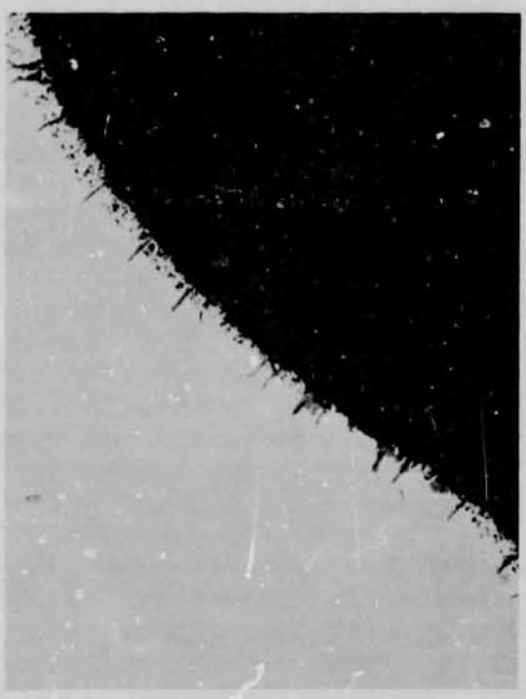


FIGURE 78. TYPICAL EROSION BARS WITH SHANKS REPAIRED BY COATING WITH S6100M OVER SILICIDE BASE



Magnification: 40X

FIGURE 79. IMPENDING SHANK FAILURE. NS-4 ON T222 AFTER 32-HOUR 2400°F OXIDATION SHANK DISCOLORATION.

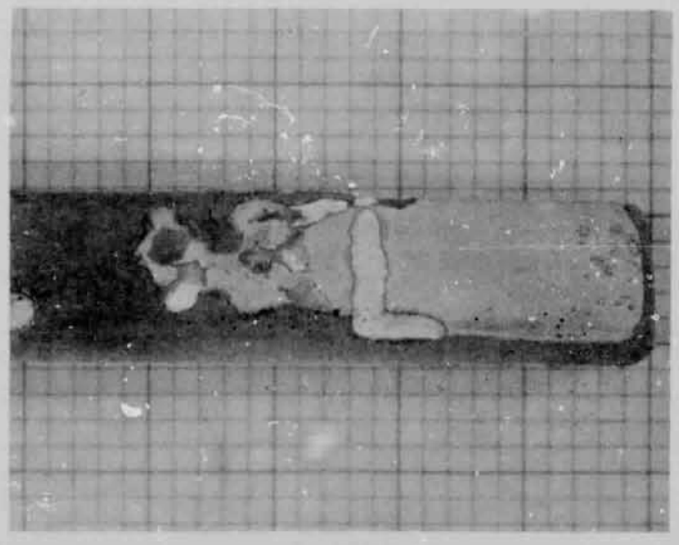
Magnification: 40X

FIGURE 80. SHANK FAILURE. NS-3 ON BLADE AND NS-26 ON SHANK ON T222 AFTER 203-HOUR 2400°F OXIDATION

While the coating has not yet failed, oxide penetration is evident and radius failure would undoubtedly develop within the next 20 hours of testing. This points out the problem (discussed in greater detail in Sec. 3.4.7) of uniform coating application. The radius failure shown in Figure 80 is apparently the result of a coating fracture becoming sufficiently large after nearly 200 hours of thermocycling to permit oxygen to penetrate between the coating and substrate silicide. The subsequent oxidation produced coating spall to the degree visible in Figure 80. The uniformity in thickness of the substrate silicide indicates that there was no severe inconsistency in the coating thickness as applied. The resulting failure occurred only after 203 hours of testing.

Blade Failure

Only one standard coating developed blade failure, and that was NS-7 on T222 (Fig. 69). This low Ti + V content coating developed severe craze cracks over the entire blade to produce the only high-temperature-zone blade failure. A second blade failure, shown in Figure 81, was more nearly an overall coating disintegration. The samples were prepared by applying a 0.001-inch thick titanium plate to the substrate over which was applied NS-4. The product was sintered at 2760° F and silicided by conventional pack methods. The resulting coating failed in eight hours of erosion testing. The coating rapidly spalled, especially from the regions where the erosion bar rested on tungsten rods during sintering. The appearance of these and other zones would indicate that excessive titanium retention produced interface regions of the very friable titanium disilicide. Rapid vaporization of interface titanium could also have produced very weak modifier layer bonding, as shown in Figure 77 and discussed previously.



Magnification: 2X

FIGURE 81. NS-4 MODIFIER OVER TITANIUM PLATED T222 AFTER 8 HOURS OF OXIDATION/EROSION TESTING OF THE SILICIDED COATING

With few exceptions, no blade or tip failures were observed in oxidation erosion tests. The blades differed only slightly in color and texture. Typical views of blades and tips are shown in Figures 82 and 83. The general appearance indicates excellent coating condition with some glass flow and beading after extended periods of testing. Unfortunately, the tests were cut short by failure in the shank region.

3.4.6 Discussion of the Test Results

The long-term cyclic oxidation tests (800 hours at 2400° F) did not prove to be sufficiently discriminating. The tests, rather, supported the observation that the majority of the coatings tested in the program would provide probably 1000 or more hours of oxidation protection when properly applied to T222 or FS-85. The tendency of the coatings on T222 to fail during very slow cooling has been suspected to be related to the titanium oxide content in the surface silicate. This supposition was supported to some degree by the observation that the highest percentage of failure (67 percent), during the accidental furnace slow cool, occurred with NS-3 (35Mo35W20Ti10V) - the highest titanium content coating tested 800 hours on T222.

The mechanical property evaluations of the coated specimens, both before and after 800-hour, 2400° F oxidation testing indicated a small loss in mechanical properties for T222 processed below 3100° F or FS-85 below 2940° F. The observed loss in strength could be largely attributed to the loss of substrate converted to silicide. The coatings, however, provided complete protection from oxygen embrittlement of the substrate.

The slow thermal cycle evaluations of selected systems indicated a reduction in oxidation resistance with excessive vanadium and titanium retention. Where the origin of failures could be determined, it was observed that the failures initiated at a specimen support spot where titanium and vanadium volatilization had been inhibited during modifier sintering. There is also the possibility that some sticking occurred to the support rods on the heavy slow cycle specimens, removing a small area of the modifier prior to siliciding.

The test most nearly simulating the actual turbine vane environment was the oxidation-erosion rig test. The most outstanding specimens in this test were the two T222 bars coated with NS-4 and sintered at 3100° F.

The major problem area in erosion rig testing was the inability to continue blade evaluation due to shank deterioration. This shank failure is a universal problem with coated refractory metals. Similar damage was observed in tests at Pratt & Whitney (Ref. 8) and TRW (Ref. 9). This deterioration must be considered separately from blade-coating failure, but in this evaluation many tests were discontinued prior to blade coating failure because of severe shank deterioration.

Magnification: 4X

FIGURE 82. NS-4 COATED T222 AFTER 221 HOURS OF OXIDATION/EROSION TESTING

Magnification: 2X

FIGURE 83. (RIGHT) NS-1 COATED T222 AFTER 96 HOURS OXIDATION/EROSION
(LEFT) NS-4 COATED T222 AFTER 221 HOURS OXIDATION/EROSION

Two divergent trends in desirable coating compositions were indicated by the rig tests. The best coatings on T222 were NS-2 (35Mo35W10Ti20V sintered at 2940° F) and NS-4 (20Mo50W15Ti15V sintered at 3100° F). Both of these coatings were low in titanium subsequent to sintering. When NS-4 was sintered at 2760° F, resulting in greater titanium and vanadium retention, there was more conspicuous craze cracking, but early shank deterioration caused a discontinuation of the tests. An evaluation of shank life indicated that high titanium content in the coating was desirable. This improvement is apparently due to increased coating strength and coating/substrate bonding. In addition, increased substrate/titanium alloying prolonged substrate life after coating fracture. The application of titanium plate to the substrate performed inconsistently. Some applications of thin titanium plate (0.0005 inch) contributed to coating protection, but where thicker applications were tested, two detrimental effects were observed:

(1) Modifier separation as a result of vaporization and possibly Kirkendall voids

(2) Residual titanium retained in the coating formed friable titanium silicide

The coating, NS-26 (20Mo40W15Ti25V), tested as a shank coating, performed exceptionally well (failure 95 and 203 hours) when tested with NS-3 on the blade section. The failures were predominantly due to inconsistency in application thickness in the overlap area rather than coating failure.

3.5 MODIFIER PROCESS VARIABLE INVESTIGATION

For the basic chemistry studies, process conditions were kept as constant as possible. This included such items as slurry vehicle (E-4), particle size (1-4 micron), and sintering time and temperature (15 hours at 2760° F). To investigate the influence of process parameters on performance, a constant chemistry, NS-1 (35Mo35W15Ti15V) was selected. The following process parameters were evaluated:

- Oxygen content of the powdered metals
- Modifier sintering temperature
- Powder particle size
- Pre-alloying of the modifier
- Activation sintering

3.5.1 Investigation of the Effect of Oxygen Content of the Metal Powders and Slip Aging

Vanadium

The present program was initiated by applying the NS-1 modifier to a set of T222 specimens. (Previously TNV-7 or NS-1 specimens (Ref. 1) had shown 2400° F lifetimes up to 1064 hours and greater than 600 hours at 1600° F.) When tested in the current program, the seemingly identical coating failed in about 16 hours of 1600° F testing. The following phenomena were investigated and systematically eliminated as explanations for the abnormal 1600° F performance:

- Contamination of the coatings by either the furnace atmosphere or the support media upon which the samples rested during oxidation
- Inadvertent deviation of the sintering temperature or coating composition from that previously used
- Impurities in the silicon

At the start of the current program, a new lot of silicon was purchased in the -200 mesh form from Keokuk Electro-Metals Company, Division of Vanadium Corporation of America. The new silicon was suspected until the same poor oxidation resistance was observed at 1600° F for specimens silicided in the silicon used in Reference 1. In X-ray fluorescence, arc emission spectrographic, and combustion analyses, the new lot of silicon was found to be purer than the older silicon. It was very interesting to note that the NS-3 (35Mo35W20Ti10V) coating yielded no failures in 200 hours of oxidation testing at 1600° F in two different experiments using the same materials and techniques that resulted in the very poor oxidation resistance for the NS-1 coating.

Restoration of the normal oxidation resistance of the NS-1 coating coincided with use of a new batch of vanadium hydride powder having a low oxygen content of <0.5 percent (conpared to ~ 4 percent characteristic of the lots of vanadium hydride powder used earlier on this program). This suggested that oxygen contamination of the vanadium hydride powder was responsible for the poor 1600° F oxidation resistance.

This possibility had been initially discounted because all vanadium hydride used in this program had been stored in an argon atmosphere; while the vanadium used in the prior program (Ref. 1), where excellent results were obtained with the TNV-7 (NS-1) coating, was stored in the air and, thus, would be expected to contain more oxygen. Unfortunately, none of the vanadium hydride used in the old program was available for analytical comparison.

Analyses of the initial lot used in this program, as well as subsequent lots, revealed the following significant differences. The first procedure for hydriding vanadium produced a product which was low in hydrogen (VH0.28) with an oxygen content < 0.5 percent. The comminution of the hydride was performed by wet milling in xylene. The initial lot was milled to produce a very fine product but with a high oxygen content (> 4 percent). The coatings prepared with this material almost consistently failed. The production of fines was subsequently minimized by shortening the 24- to 48-hour grinding time to 6 to 8 hours and by removing fines through the batch settling techniques. The resulting product has coarser material and an oxygen content near 0.5 percent.

The hydriding process was changed from the one described in Reference 1 to the procedure in Appendix B. By allowing longer time for hydriding and slower cooling in hydrogen, it was possible to produce a lower oxygen (0.2 percent oxygen), higher hydrogen (VH0.7) product. This hydride was significantly more friable allowing the material to be easily milled to produce a stable powder product with < 0.5 percent oxygen.

Titanium

The early failure (< 200 hours) at 1600° F of certain modifier compositions (especially NS-6) containing the new lot of low oxygen (0.5 percent oxygen) content vanadium led to suspicion of the oxygen content of the titanium powder. Although the titanium powder was low in oxygen content (< 0.5 percent oxygen) prior to milling, the actual composition when applied was unknown. To attempt to reduce the potential source of oxygen contamination, titanium sponge (0.06 percent oxygen) was hydrided without increasing the oxygen content and added to the mill mixture in this condition. The resulting slip would be lower in oxygen content due to the lower content in the starting material and also due to increased friability and stability toward oxidation of the titanium hydride as compared to titanium powder. The resulting slips produced coatings with greatly reduced low-temperature failures.

The lot of pre-alloyed NS-1 modifier alloy, although not extensively tested, contained 0.14 percent oxygen and proved to be satisfactory in oxidation resistance.

Slip Aging

To evaluate the shelf life of the NS-series slips (including oxidation stability), one set of oxidation specimens each of T222 and FS-85 were tested with aged modifier slip. A modifier coating of NS-23 was applied using slip that had been stored for 70 days. The products when processed together with samples coated with freshly prepared slip showed no detectable difference in performance. This experiment supports the premise that slips may be prepared and stored for short periods of time in glass jars purged with argon prior to sealing.

3.5.2 Sintering Temperature Study

The effect of variation of the sintering temperature on the oxidation resistance was investigated for the NS-1 coating. Sintering temperature variation between 2665 and 2860° F appears to have little effect on the oxidation resistance of the resultant coating, as indicated in Table XXII. Metallographic studies revealed that as-sintered microstructure (hot epoxy impregnated before polishing) was virtually independent of the sintering temperature. Porosity was determined by boiling the as-sintered specimens in toluene for one and one-half hours prior to cooling to room temperature. The specimens were blotted with a paper towel moistened in toluene before being weighed on an analytical balance. The coating sintered at 2665° F had 37 percent porosity and the coating sintered at 2860° F had 33 percent porosity. An attempt was made to measure the hardness of the unpolished as-sintered coatings; DPH indentations (200 to 1000 gram loads) were so irregular as to be unreadable, and Rockwell 15 N values were not reproducible.

TABLE XXII

RESULTS OF SINTERING TEMPERATURE STUDY FOR NS-1 COATING ON T222

Sintering Temperature (° F) (A) (B)	Oxidation Lives	
	Hours at 1600°F	Hours at 2400°F
2665	3 at >209	167, 2 at >207
2765	3 at >209	3 at >209
2860	3 at >209	3 at >209

(A) Titanium added as TiH_2; 2765 F is standard sintering temperature

(B) Time was 15 hours for all runs.

The effect of sintering temperature was further evaluated for temperatures as low as 2200° F by the use of sintering aids and as high as 3100° F. The effect of this broad temperature range is a change in coating chemistry and structure resulting in a significant alteration in performance.

Using weight loss data during sintering for the NS-1 and NS-4 coatings, it was calculated that the following amount of Ti + V was retained after sintering for 15 hours at various temperatures:

Sintering Temperature (° F)	Percent Ti + V in Coating After Sintering	Percent Ti + V Lost During Sintering
2200	30	0
2760	18	40
2940	12	60
3100	5	83

The above calculations were made using the assumption that the weight loss was all due to the vaporization of the binder plus vanadium and titanium. Calculations of the rate of loss by vaporization of Mo, W, Cb and Ta, using the Langmuir vaporization equation and the vapor pressure from Nesmeyonov (Ref. 6), Figure 84, showed a negligible loss for these elements at 3100° F in 15 hours. Conversely, at an activity of one, titanium vaporizes at 0.001 inch per hour at 2760° F and 0.009 inch per hour at 3100° F, and vanadium at 0.0002 inch per hour at 2760° F and 0.004 inch per hour at 3100° F. Due to alloying and configuration effects, vaporization will be somewhat slower than theoretically estimated. The data on vaporization plus performance data show that the desirable composition of the modifiers (NS-1 and NS-4) is not 70%(W+Mo) plus 30%(V+Ti), but rather 85 to 95%(W+Mo) plus 15 to 5%(V+Ti). The coatings evaluated with the 70-30 composition "as-tested" (NS-11 and NS-12 nickel activated coatings and NS-13, a palladium-activated coating sintered at 2200° F) glassed excessively at 2400° F. Surface analysis showed the NS-13 coating to have three times the titanium and two times the vanadium of a typical NS-1 coating sintered at 2760° F. The extra quantities of these elements were undoubtedly the cause of the poor performance. The two coatings evaluated with the 95-5 composition "as-tested" (NS-3 and NS-4 on T222 erosion bars sintered at 3100° F) produced inconclusive results. The NS-3 coated specimens failed too early due to shank deterioration to evaluate the hot wedge portion. The two NS-4 coated bars gave the most outstanding results of the program with erosion rig lives of 207 and 221 hours.

3.5.3 Modifier Alloy Particle Size Study

The standard procedure for preparing the spraying slip includes adding 5 micron tungsten, 5 micron molybdenum, -20 +50 mesh titanium hydride (which is very friable), -325 mesh vanadium hydride (which is reasonably friable), and the E-4 vehicle to a ball mill. The standard practice of ball-milling the slip for 20 hours yielded an average particle size of 2 microns for the NS-1 alloy. This was obtained by the Fisher subsieve procedure with the ASTM designation B330-65.

The dry powder used in the subsieve analysis was obtained by centrifuging quantities of a slip (12-inch diameter, 2200 rpm centrifuge). This was followed by one xylene rinse and two acetone rinses, using centrifugation to recover the maximum

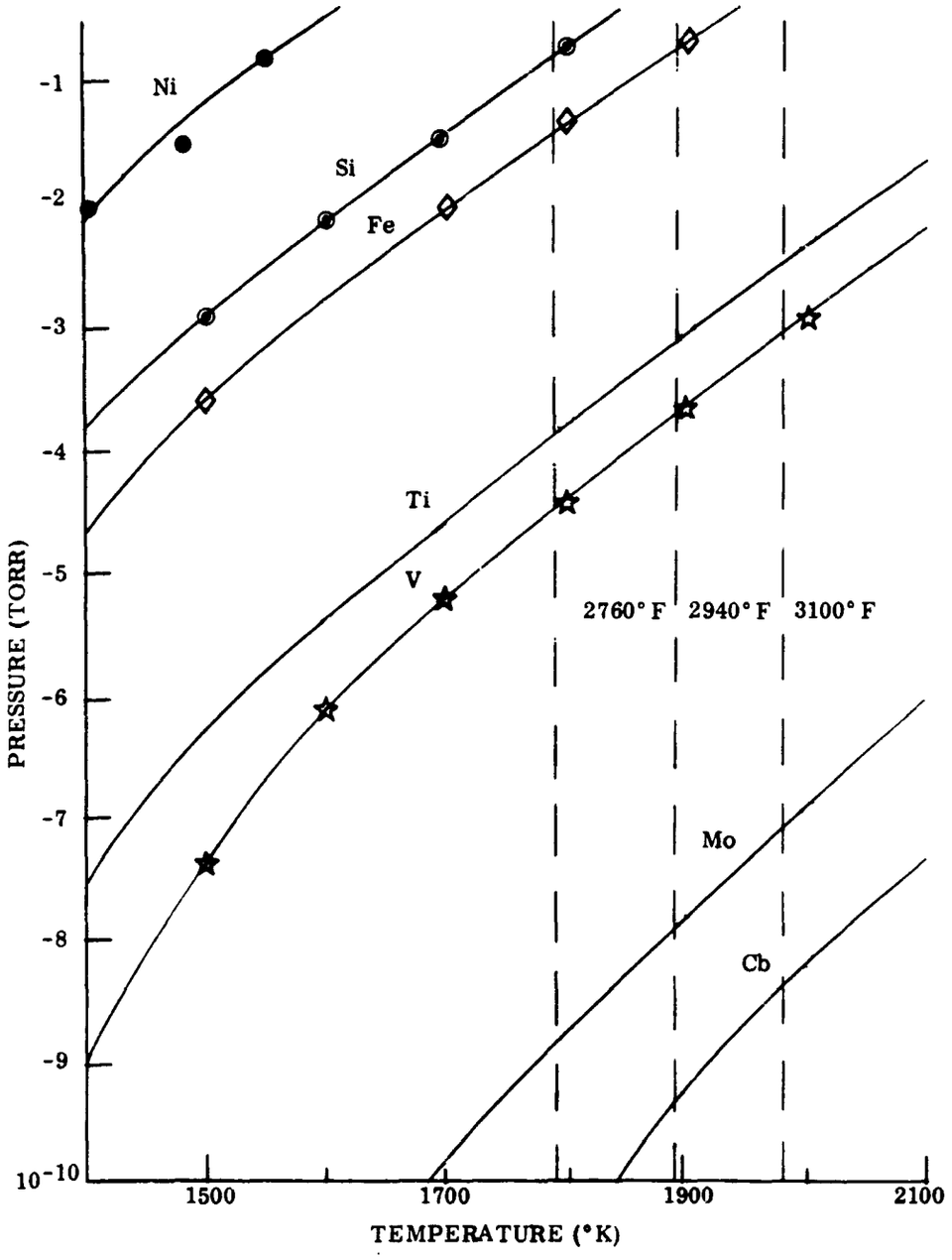


FIGURE 84. VAPOR PRESSURE VERSUS TEMPERATURE FOR VARIOUS ELEMENTS

quantity of the particles in the slip. Less than 1.4 percent of the particles could not be recovered by centrifugation. Replacement of the 5 micron tungsten by 0.74 micron tungsten, with the standard 20-hour milling time and, also, longer milling times were investigated.

Use of the 0.74 micron tungsten in conjunction with the standard 20-hour ball milling yielded an average Fisher subsieve particle size of 1.14 microns. Ball milling the 5 micron molybdenum, -325 mesh vanadium hydride and -20 + 50 mesh titanium hydride, for 65 hours before adding 0.74 micron tungsten, followed by an additional 20 hours of milling, yielded a particle size of 0.9 micron. The slip with the 0.9 micron particle size was very difficult to spray, even after dilution to a fluid-to-solids ratio of 4.5. The slip behavior suggested that, although the average particle size was 0.9 micron, some of the fines were probably in the colloidal range. The poor spraying characteristic of the 0.9 micron slip was possibly the major cause of the poor 1600° F oxidation resistance reported in Table XXIII.

Dipping slips were prepared as described in Section 3.7.2. This includes adding 5 micron tungsten, 5 micron molybdenum, -20 +50 mesh titanium hydride, -325 mesh vanadium hydride, and xylene to a ball mill. Two slips were prepared by milling for 22 and 60 hours, respectively. The modifier powders were then blended with vehicle for application. The average particle size obtained by the Fisher subsieve measurement was 6.7 and 3.2 micron, respectively. The early failure (at 8 hours) of specimens dip coated with the coarsely milled modifier can be directly attributed to the large particle size which produced an excessively segregated coating. The 3.2 micron particles produced a coating that failed due to problems in dipping techniques. The results indicate that an average particle size of 3.2 microns or less is satisfactory for elemental powders when sintered 15 hours at 2760° F.

Table XXII also reveals that the sintering temperature can be safely reduced to 2560° F when the 0.74 micron tungsten powder is used in conjunction with the standard ball milling time of 20 hours. The benefit of using the 0.74 micron tungsten instead of the standard 5 micron tungsten is not well established, however. Review of the sintering temperature study in the preceding section reveals that good oxidation resistance was obtained when coatings prepared with 5 micron tungsten were sintered at 2650° F; the use of 5 micron tungsten in conjunction with a 2560° F sintering temperature was not investigated experimentally.

It is interesting to note that the 5 micron tungsten costs approximately $4.50 per pound and contains approximately 250 ppm oxygen, while the 0.74 micron tungsten costs approximately $5.50 per pound and contains approximately 2500 ppm oxygen. The higher oxygen content of the finer tungsten does not appear to affect the performance of the coating so long as oxygen content of the other slip components is low, but adds to contamination of the vacuum furnaces. The finer tungsten is currently not recommended as a substitute for 5 micron tungsten.

TABLE XXIII

MODIFIER-ALLOY PARTICLE-SIZE STUDY
OXIDATION TEST RESULTS (SILICIDED NS-1 COATING)

Slurry Preparation	Average Particle Size	Sintering Temperature (°F) (1)	Oxidation Lives	
			Hours @ 1600°F	Hours @ 2400°F
• 5μ Mo, -325 mesh VH_x, -20+50 mesh TiH_2, 5μ W • Ball milled 22 hours • Fluid/Solids = 1.6	6.7μ	2760	2 @ 8 (2)	-
• 5μ Mo, -325 mesh VH_x, -20+50 mesh TiH_2, 5μ W • Ball milled 60 hours • Fluid/solid = 2.4	3.2μ	2760	2 @ 190 (2)	-
• 0.74μ W, 5.2μ Mo, -325 mesh V-H, -20+50 mesh TiH_2 • Ball milled 20 hours • Fluid/solids = 2.5	1.14μ	2765	3 > 237	2 @ 20, > 237
		2560	3 > 237	3 > 237
• 5.2μ Mo, -325 mesh VH_x, -20+50 mesh TiH_2 • Ball milled 65 hours; 0.74μ W added and ball milled additional 20 hours • Fluid/solids = 4.5 • Sprayed poorly	0.9μ	2560	108, 128, >237	3 > 237
		2455	128, 2 @ 148	3 > 237

Notes: 1. All samples vacuum sintered 15 hours.
2. Dip coated.

3.5.4 Pre-Alloying the Modifier

The use of a pre-alloyed powder instead of a mixture of elemental powders was considered to have the potential for enhancing the inherent oxidation resistance of the silicided modifier alloy by providing a more homogeneous coating. However, reduction of the activity of the titanium and vanadium would be expected to reduce the rates of vaporization of these materials and also their driving force for diffusion into the outer layers of the substrate. The NS-1 modifier alloy was obtained in pre-alloyed form from the Wah Chang Corporation, Albany, Oregon (see Sec. 3.1 for details of the powder).

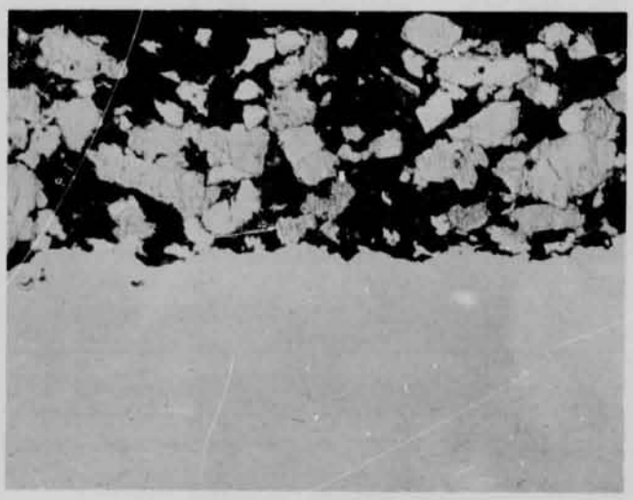
Fisher subsieve particle size of the as-received powder was 13.4 microns; after ball milling for 20 hours in the E-4 vehicle, the particle size dropped only to 12.5 microns as compared to 1.95 microns for the powders in the NS-1 slip after milling for the same period of time (Sec. 3.4.3). The 20-hour ball milling operation is thus more of a mixing than comminution operation, except for the friable hydride materials.

A suspension of the -325 mesh pre-alloyed powder in the standard E-4 vehicle showed good spraying characteristics; however as related to the standard NS-1 modifier alloy slip, it showed a greater tendency toward settling, which was attributed to the larger particle size. The as-sintered (2765° F for 15 hours) and as-silicided weight gains for the pre-alloyed modifier alloy were virtually identical to those of the conventional modifier alloy obtained by mixing elemental powders. The specimens had a satisfactory appearance, but noticeably coarser texture due to the larger particle size. The microstructures of the as-sintered and as-silicided coatings are shown in Figure 85. The larger particle size of the pre-alloyed modifier alloy and the lack of homogeneity are readily apparent. Diffusion of titanium and vanadium into the substrate during sintering is approximately the same as for the unalloyed NS-1 modifier.

While oxidizing the silicided coatings, the samples displayed a normal black matte appearance at 1600° F, but developed a yellow powdery appearance between 24 and 40 hours. This discoloration later vanished and there were no failures in 209 hours of furnace testing. At the end of two hours of oxidation at 2400° F, numerous collapsed glass bubbles were found on the surface of all three specimens, as shown in Figure 86. As the 2400° F oxidation tests continued, these collapsed glass bubbles were absorbed by the coating and no failures were observed at 209 hours of testing.

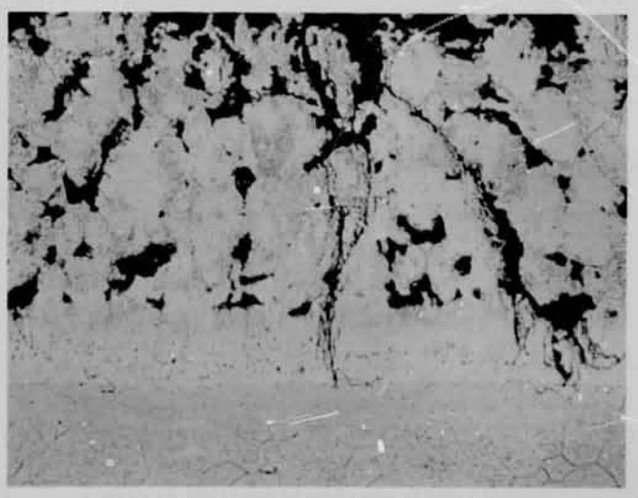
3.5.5 Discussion of Modifier Process Variables

As a result of the investigation of process variables, several observations were made. It was found to be essential that the oxygen content of the powdered metals be retained at as low a level as possible. For vanadium, it was proven essential that for a V/Ti weight ratio equal to or greater than one, the oxygen content must be equal



As-Sintered

Magnification: 250X



As-Silicided

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FIGURE 85. PREALLOYED NS-1 MODIFIER ALLOY

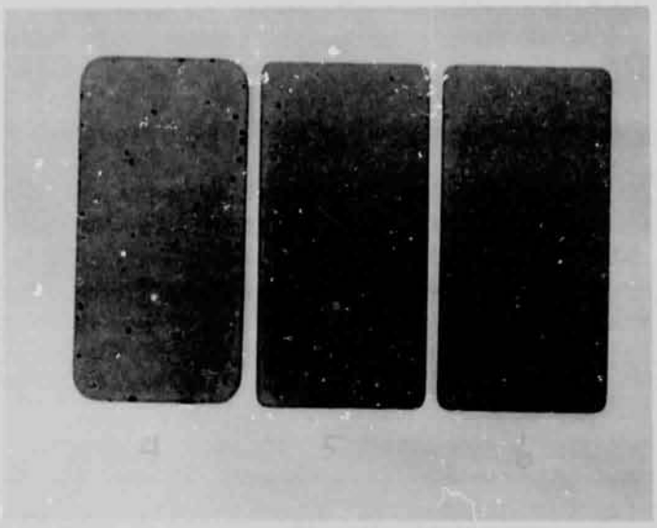


FIGURE 86. SPECIMENS PROVIDED WITH PRE-ALLOYED NS-1 MODIFIER ALLOY, AND THE SILICIDED SPECIMENS OXIDIZED FOR TWO HOURS AT 2400° F SHOW COLLAPSED GLASS BUBBLES

to or less than 0.5 percent. It was observed that coatings performed better when prepared using titanium hydride (0.06 percent oxygen) rather than powdered titanium (0.3 percent oxygen). The exact mechanism of the effect of oxygen to reduce coating protection was not determined. An oxygen level of 0.2 percent for the total modifier prior to milling of the slip was acceptable and 0.3 percent was unacceptable. The pre-alloyed material with 0.14 percent oxygen fell within the satisfactory range and produced an acceptable coating.

The increase in sintering temperature tended to decrease coating porosity and to increase the bond to the substrate, but excessive temperature caused substrate grain growth, reducing strength. At 2760° F and above, the total loss of iron as well as most of the titanium and some of the vanadium was observed. Thus, the sintering temperature has a significant effect on the modifier chemistry as well as structure.

The size of the elemental powders was observed to be satisfactory to produce a consistent coating with an average particle size equal to or less than 3.2 microns. However, pre-alloyed powders could be used to 12.5 microns diameter. For the spray application of the modifier, an average particle size less than one micron proved to be unworkable.

3.6 SILICON/MODIFIER RATIO INVESTIGATION

The NS-1 modifier alloy was applied to T222 in thicknesses equivalent to 33, 68 and 112 mg/cm^2. A standard siliciding cycle resulted in further weight gains of

32, 46, and 52 mg/cm^2, respectively. Table XXIV contains a summary of the oxidation results of the silicided specimens. Early failures were observed where there was insufficient silicon to completely penetrate the modifier alloy layer. The poor 2400° F oxidation performance, experienced at a silicon/modifier ratio of 2.07, can be explained only on the basis that slight non-uniformities in thickness of the modifier layer allowed some regions to be incompletely silicided although sufficient silicon was present to yield an average silicon/modifier ratio to correspond to complete penetration. In this regard, it was interesting to note that for experiments T_2-185 and T_2-303 (Ref. 1), the TNV-7 (identical to NS-1) coating yielded excellent oxidation resistance for silicon/modifier ratios of 2.20 and 2.07.

TABLE XXIV

RESULTS OF SILICON/MODIFIER ALLOY-RATIO STUDY
FOR NS-1 COATING ON T222

Modification Gain (mg/cm^2)	Siliciding Gain (mg/cm^2)	Silicon/Modifier Atomic Ratio	Oxidation Lives	
			Hours at 1600° F	Hours at 2400° F
33	32	2.98	2 @ 209, >209	3 @ 207
60	44	2.23	3 @ >209	3 @ >209
68	46	2.07	3 @ >209	20, 40, 167
112	52	1.41	3 @ 2	3 @ 2

3.7 DIPPING STUDIES AND HOLLOW VANE CONFIGURATION EVALUATION

The ultimate objective of this program was the development of a coating or family of coatings for turbine vanes or blades. A coating must, therefore, provide protection to both the internal as well as external surface of hollow vanes. Coating the internal surfaces of hollow vanes, which are inaccessible using spray techniques, required the development of an alternate coating method. The system selected as offering the greatest versatility and promise of success was the dipping process. Prior to the current program, the interior and exterior surfaces of T222 hollow box beams were coated with NS-1 (Ref. 3) (beam dimensions 0.6 x 0.6 x 5 inches, and either 0.030 or 0.060 inch wall thickness). After siliciding, the coated beams were subjected to compression tests of 130 minutes at 2800° F, or 30 minutes at 3000° F, with no noticeable coating deterioration. Thus, the potential for the slurry coating by dip application was clearly demonstrated.

In the present program, the NS-1 coating was taken as a standard composition to develop dip coating technology for application to simulated hollow vane configurations.

3.7.1 Preliminary Experiments

In the initial investigation, the NS-1 coating was applied to the airfoil specimens which were formed by bending 0.030-inch T222 sheet and TIG welding the trailing edges. The inner surfaces were dipped and the exterior surfaces were sprayed.

The slip composition used to dip the interior of the airfoil was as follows:

TiH_2 (-20 +50 mesh)	120 gm
W (3 to 9 micron)	280 gm
VH_x (-325 mesh)	120 gm
Mo (3 to 7 micron)	280 gm
E-4 vehicle	120 ml
Milling Time	20 hours
Specific Gravity	3.81
Viscosity	20 seconds, No. 2 Zahn cup

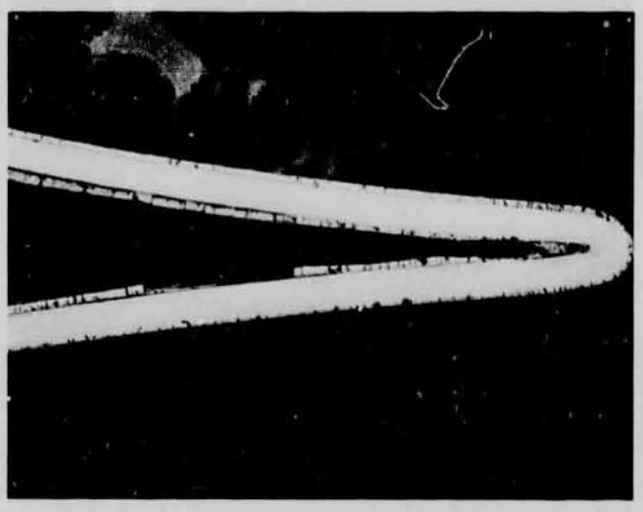
A double-dip procedure was used with one minute between dips. After each dip the specimen was allowed to drain and the excess was removed from the drained end with a spatula. The exterior surfaces were brushed free of coating and sprayed in the standard manner. The weight gain on the interior surfaces of the four airfoil sections ranged from 54.6 to 70.2 mg/cm^2. Both modifier and silicon weights were within the normal range for the NS-1 coating.

In oxidation tests at 1600° F and 2400° F, the airfoil section failed in two hours at each test temperature. The failure was on the flat inner surfaces, coated by dipping, and was well removed from the trailing edge. Figure 87 shows the failure area on the specimens oxidized at 2400° F. Although silicon appears to have completely penetrated the modifier alloy in the failure area, penetration was not complete in the faying area at the trailing edge of the airfoil specimen, as can be seen in Figure 87. Although failure did not take place in this unsilicided modifier alloy during the short 2-hour oxidation period, failures would be probable in this area as the oxidation lives of the airfoil samples are increased.

3.7.2 Vane Configuration and Joining Techniques

Airfoil Shape Development

The preliminary dip coating evaluation indicated the necessity for increasing the interior radius of curvature of the vane trailing edge. Eight hollow airfoil shapes



Entire Trailing Edge

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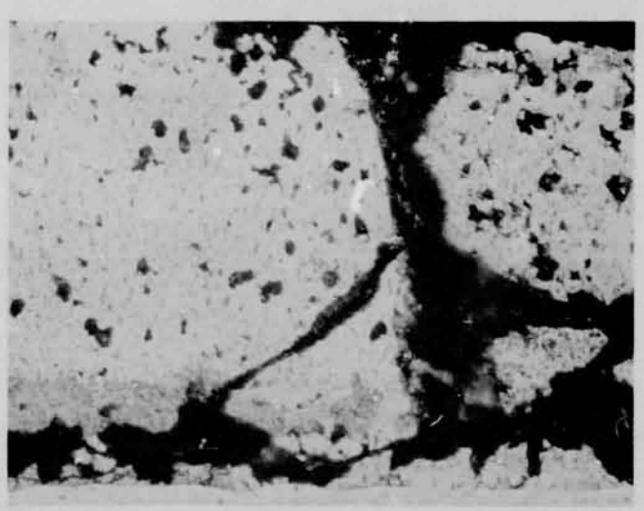
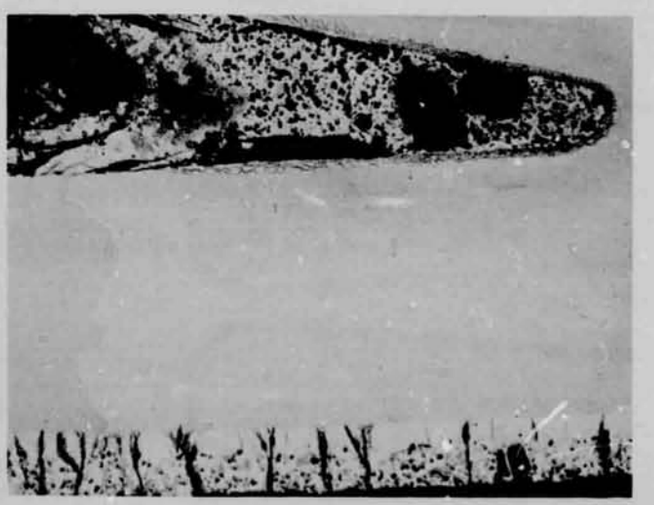


Failure Area

Magnification: 250X



Faying Area

Magnification: 50X

FIGURE 87. NS-1 COATED HOLLOW AIRFOIL SPECIMEN OXIDIZED TWO HOURS AT 2400° F

were fabricated and evaluated to optimize sample configuration. These shapes, shown in Figure 88, were joined by either fusion welding or diffusion bonding at the trailing edge. Fusion welding was found to be unsatisfactory due to the difficulty in producing smooth, uniform, crack-free internal surfaces.

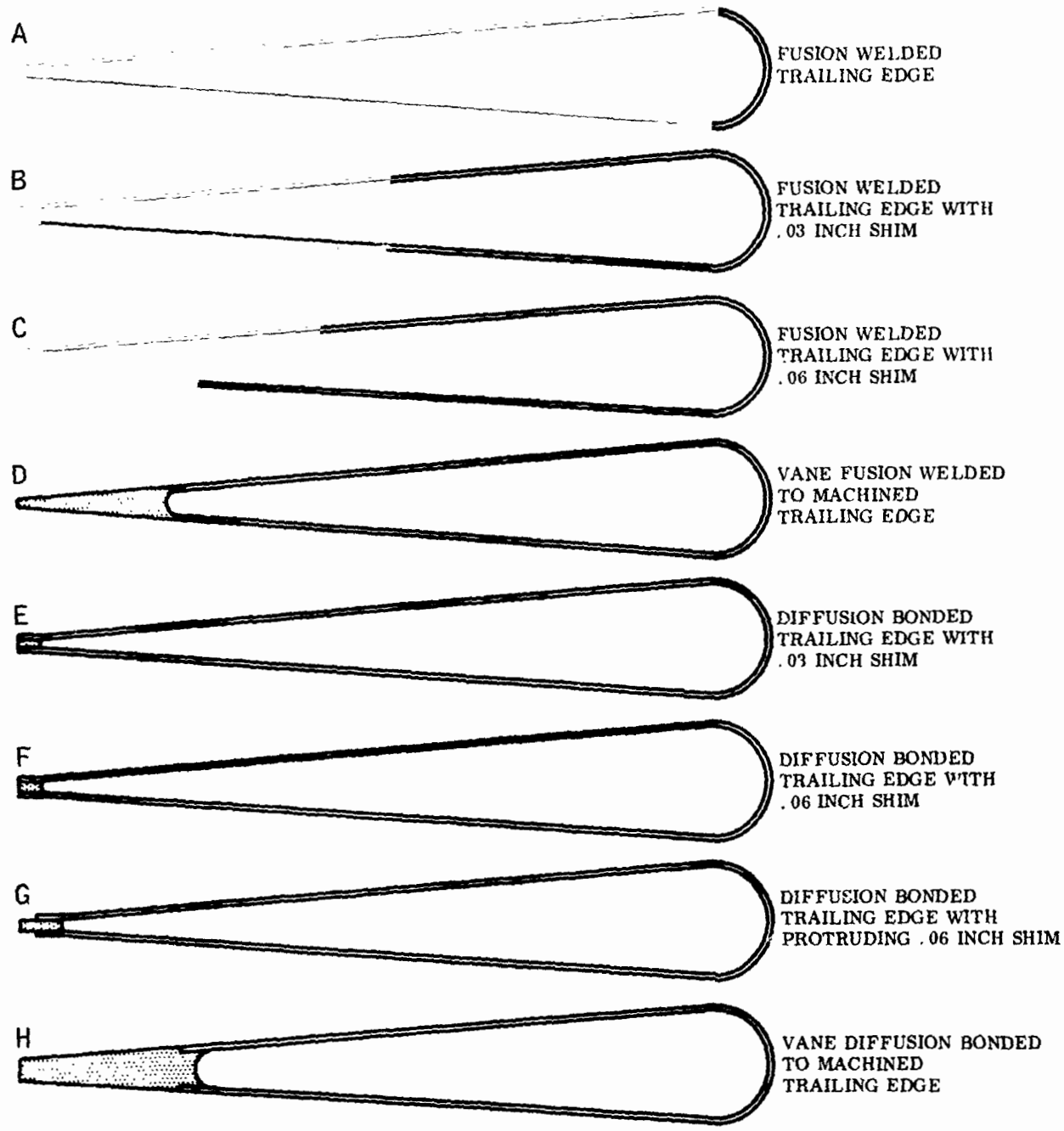


FIGURE 88. EVALUATED AIRFOIL SHAPES

The coating evaluations of the various vanes revealed that an interior radius of curvature of 0.015 inch or less for the trailing edge of vanes A, B and E was too small. The applied coatings were non-uniform due to excessive coating retention in the sharp re-entrant angle. The C and D configurations could be successfully coated; however both were difficult to fabricate with smooth, crack-free internal surfaces. The internal weld bead served as a surface discontinuity, which was a potential source of surface cracks or flaws that could be deleterious to the coating. The diffusion bonded F, G and H configurations were successfully coated; however H was excessively expensive to machine. The F and G forms were both acceptable, with G being easily machined after bonding to produce the desired trailing edge radius.

The studies also revealed that a more uniform deposition as well as improved coating adherence could be produced by grit blasting all internal surfaces prior to assembly. Samples which were grit blasted prior to assembly developed no more internal than external failures. Vane surfaces that were not sandblasted internally provided inadequate bonding between coating and substrate so that failures often occurred on internal flat surfaces.

3.7.3 Vehicle Development

Initial dipping activities emphasized the use of a Solar vehicle (E-4) and control of the specific gravity to effect set and viscosity control in application of the NS-1 modifier coating to internal surfaces of simulated vane shapes. This early work showed that the small amount of residual N-200 ethyl cellulose, at a liquid-to-solids volume 1.6 to 2, appeared to be inadequate to provide support for the heavy bisque. Lower viscosity grades were investigated in an effort to retain ethyl cellulose-to-solid ratio equal to or greater than that in the spray coating at the decreased liquid-to-solid ratio in the dipping slips.

Three grades of ethyl cellulose were evaluated (N-7, N-22 and N-200). Vehicle solutions were prepared by blending the required amount of each binder with xylene in a glass container for 16 hours on a conventional rolling mill. After allowing the solution to stand for 4 hours, viscosities were determined by the Zahn Cup Test method using the No. 2 cup. The results are plotted in Figure 89. At the 5 gram per 100 milliliter concentration (hereafter referred to as 5 percent solution), the following results were observed:

- The N-200 ethyl cellulose solution was not homogeneous, but separated into a clear, thick gel-like phase and a viscous liquid phase
- Both N-22 and N-7 solutions were homogeneous clear liquids

Viscosity measurements of the N-7 and N-22 solutions were 18 and 125 Zahn seconds, respectively. The viscosity of the 5 percent N-200 solution was not determined.

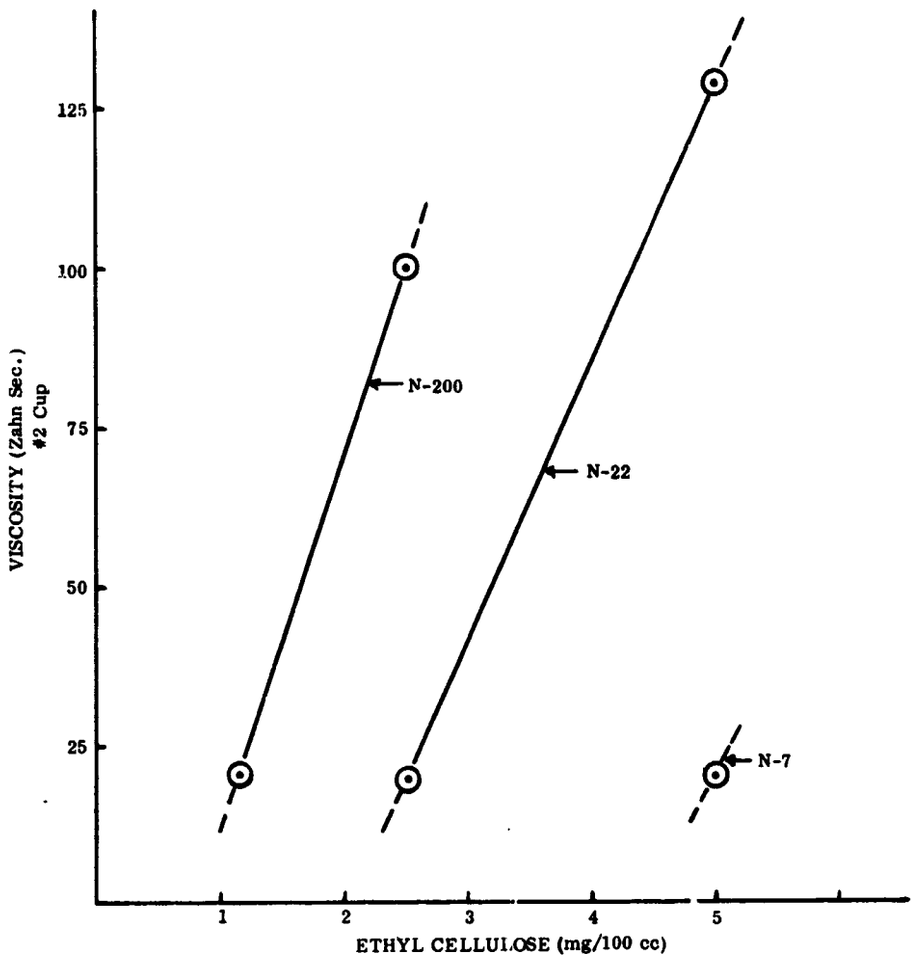


FIGURE 89. RELATIVE VISCOSITY OF ETHYL CELLULOSE/XYLENE SOLUTION

Viscosity measurements of solutions (2-1/2 gm/100 ml xylene) averaged 20 and 100 Zahn seconds for the N-22 and N-200 binders, respectively. The viscosity of 2.5 percent N-7 binder was too low to be effective in the program and was not measured.

A vehicle viscosity of 25 Zahn seconds (No. 2 cup) was found to give adequate suspension. A viscosity less than 25 seconds was observed to provide inconsistent coating retention indicating the formation of a solvent-rich surface layer which subsequently washed the specimen during withdrawal. A 5 percent ethyl cellulose solution was observed to give more consistent deposition with respect to solution age than a 2.5 percent solution. The 5 percent was also found to provide the desired bisque support in the low vehicle to solids ratios required for the slip.

Three solvents (xylene, xylene-20 percent secondary butyl alcohol and acetone) were evaluated for use in the vehicle.

The acetone was included to increase vehicle volatility which should, in turn, increase bisque retention by increasing the set of the slip, particularly on internal surfaces. Normally the internal deposition is about two-thirds the external deposition. The tests revealed that "shorelining" was a significant problem with the acetone containing slip, and there was no improvement in internal to external deposition.

The xylene-20 percent secondary butyl alcohol was of interest in that it dissolves the ethyl cellulose more readily than the pure xylene. The xylene-alcohol-ethyl cellulose product is clearer and of lower viscosity than the equivalent xylene-ethyl cellulose mixture. The slip evaluations revealed no significant improvement in slip performance with the alcohol addition. The pure xylene had the advantage that evaporated solvent could be replaced without disturbing the solvent ratio as in a two-component solvent system.

The vehicle was, therefore, fixed at xylene-5 percent ethyl cellulose, utilizing 3 gm N-7 and 2 gm N-22 per 100 ml xylene to provide the preferred viscosity.

3.7.4 Rate of Withdrawal

The rate of withdrawal was investigated utilizing a variable speed, mechanical withdrawal unit (Fig. 90) because manual withdrawal had given inconsistent results. The thickness of the dipped coating is increased as withdrawal speed increases; however an excessive withdrawal rate produces runs and sags. The rate of withdrawal without optimizing for a specific slip was found to be satisfactory for the slips of interest at 0.05 inch/second. All slip comparison tests were conducted at this withdrawal rate. For the NS-1 slip of 3 micron average particle size, the effects of withdrawal rate on deposition are shown in Table XXV.

TABLE XXV

EFFECT OF VEHICLE/SOLID RATIO ON BISQUE RETENTION DIP COATED FROM 3 MICRON AVERAGE PARTICLE SIZE SLIP

Slip Density	Vehicle/Solid Ratio	Deposit at a Withdrawal Rate of	
		0.05 in/min in mg/cm^2	0.02 in/min in mg/cm^2
3.7	1.8	250 ± 10	160 ± 10
3.5	2.1	110 ± 10	110 ± 10
3.3	2.4	80 ± 10	80 ± 10

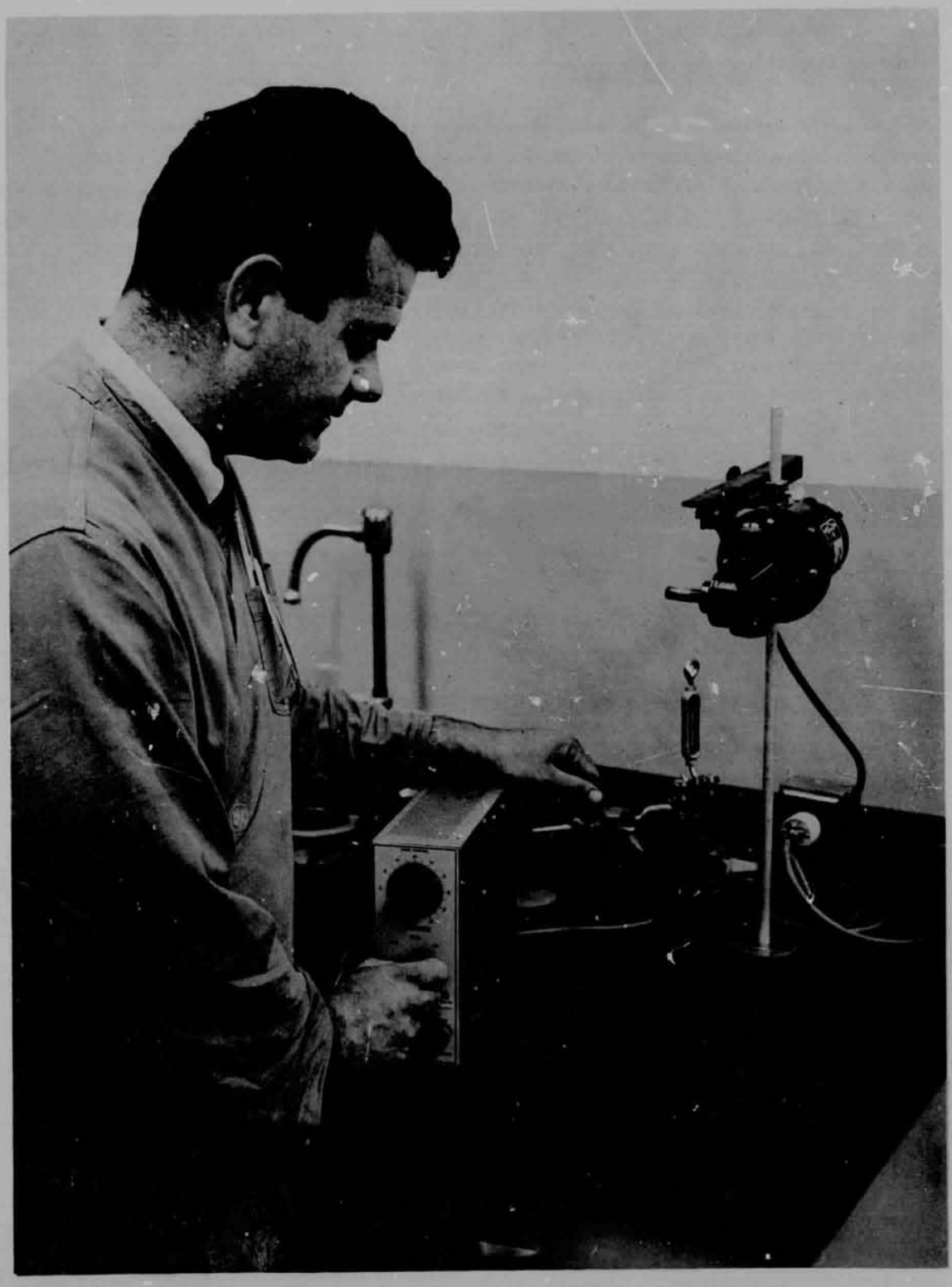


FIGURE 90. VARIABLE SPEED DIP COATING WITHDRAWAL UNIT

Determination of Effects of Vehicle/Solid Ratio and Particle Size

The relation of the vehicle/solid ratio to slip density was determined both theoretically and experimentally. There was no observed deviation between the two evaluations. The experimental data are plotted in Figure 91. This graph was used to monitor slip composition as vehicle was added to the test slip to obtain a product which would give the desired bisque weight on dipped samples.

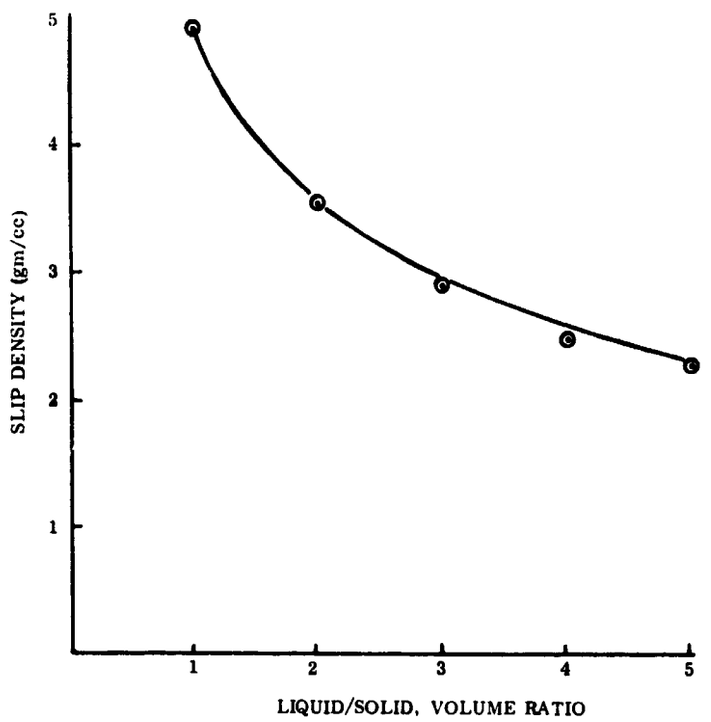


FIGURE 91. EFFECT OF VEHICLE/SOLID RATIO ON NS-1(D) SLIP DENSITY

The initial studies attempted to fix particle size only by specifying the hours of milling time. As the slip specifications became more closely fixed, the need for particle size control became more acute. Particle sizes were determined utilizing a Fisher subsieve analyzer.

Slips were prepared using metal powders of the NS-1 composition milled 6, 22, and 60 hours in pure xylene. The slip was filtered, vacuum dried and blended with vehicle to form slip with a liquid-to-solid volume ratio of 1.6:1 to produce slip with a density of 4 gm/cm^3. This liquid-to-solid ratio, when prepared with powder milled 6 hours, produced slip with satisfactory draining characteristics; but with

powder milled 60 hours, the slip was too viscous for dipping.

The effect of specimen withdrawal rate on the bisque weight using the 6-hour slip was determined. The bisque weight was 24 mg/cm^2 at a withdrawal rate of 0.05 inch/minute and 17 mg/cm^2 at a withdrawal rate of 0.02 inch/minute. These bisque weights were well below the 70 mg/cm^2 desired for the NS-1 coating; so the slip was considered unsatisfactory for coating.

The 22-hour slip (6.7 micron average particle size), with a liquid/solid ratio determined to be 1.6:1, had satisfactory draining characteristics yielding a dip bisque retention of 40 mg/cm^2 at a withdrawal rate of 0.005 inch/minute. This slip was used to coat two plates and four vanes. Three vanes were coated by dipping alone, and one was coated by dip coating internal surfaces and spraying the exterior.

For the 60-hour slip (3.2 micron average particle size), the bisque weight for various liquid/solid ratios and withdrawal rates are shown in Table XXV. The results show that a vehicle-to-solid ratio of 2.4 to 2.5 produces the desired bisque weight. This slip was used to coat two flat specimens and four vanes for oxidation tests. Two vanes were coated by dipping, alone, and two were coated by a combination of dip coating internal surfaces and spraying the exterior.

With external spraying it was difficult to obtain adequate bonding between the internal dipped coating and the external spray. Specimens that appeared satisfactory after being sintered developed flaws in the siliciding operation. Two typical sample vanes are shown in Figure 92. A spray joint flaw, developed during siliciding, is pictured in Figure 93.

The complete dip coating of specimens was accomplished utilizing the controlled withdrawal rate unit. A specimen was suspended between needle points and dipped into and withdrawn from the slip, as shown in Figure 90. The flaws left by the needle points were brush repaired. This repair was accomplished by brushing the dipping slip, thinned about 50 percent with secondary butyl alcohol, directly on the defective area. After drying, the brushed-on bisque was sanded flush with the dip coating.

All of the vanes and coupons coated with the 3.2 and 6.7 micron particle size slips were silicided to a silicon-to-modifier atomic ratio of 2.1 to 2.3. These specimens were then oxidation tested at 1600° F, the temperature found to be most severe on these coatings. All specimens survived 2 hours. Specimens coated with the coarser slip failed during the first 8 hours. The specimens coated by dipping with the finely milled slip, only, survived much longer. One flat plate coated with the finely milled slip failed in 8 hours, while the other developed a pinhole after 166 hours. The two totally dip-coated vanes each developed a pinhole in 190 hours at 1600° F. Both vanes are shown in Figure 94 with the macro and microstructures pictured in Figures 95 and 96. The macro shows the general uniformity of the dipped coating with acceptable

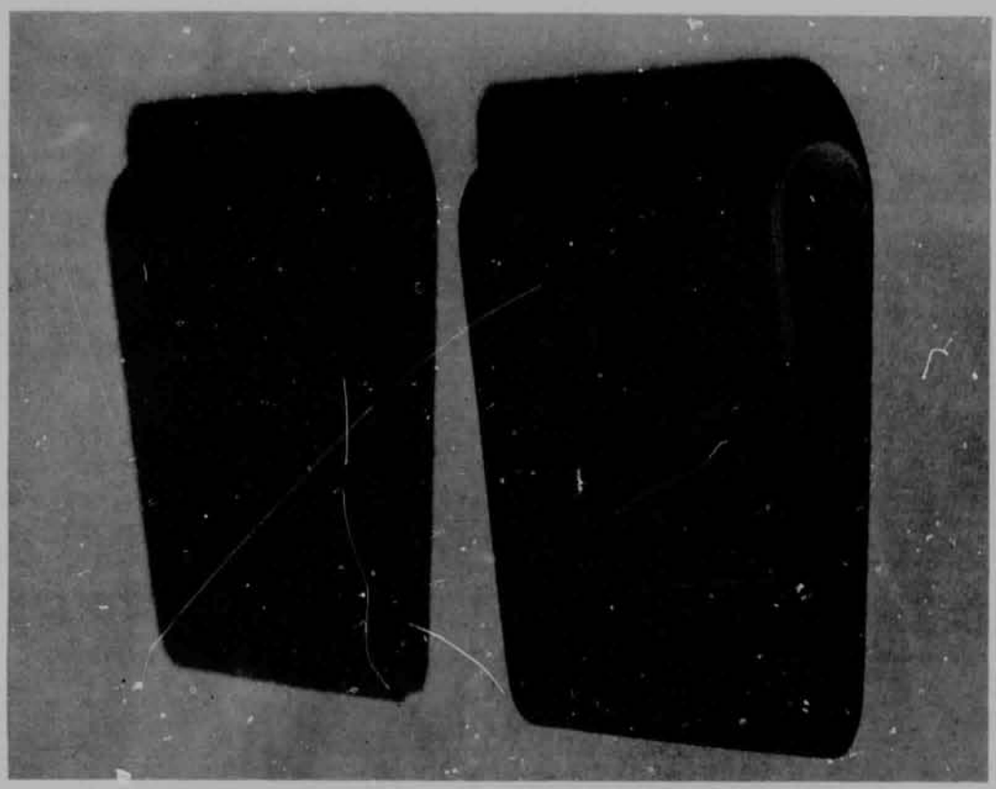
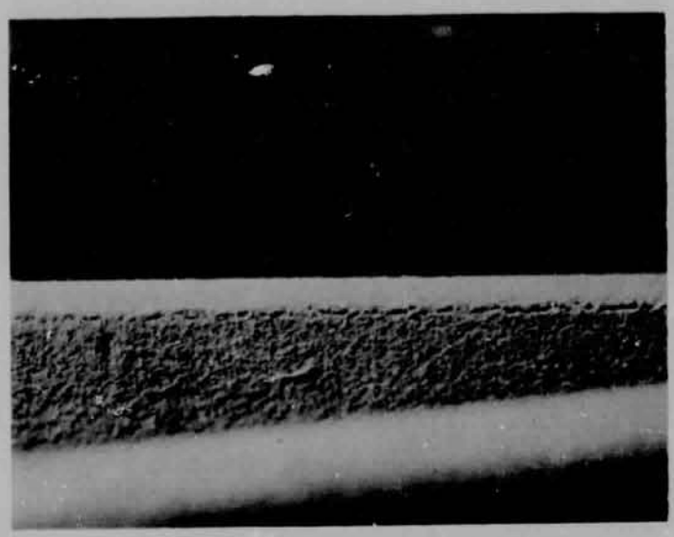


FIGURE 92. TYPICAL DIPPED SIMULATED VANES

uniformity in the internal trailing edge. The micro shots show that the upper withdrawal edge was excessively thin in modifier while the drain edge is excessively thick. One vane slowly developed edge failure on the thinly coated upper edge, shown in Figure 94, after 190 hours of testing. The other vane showed initiation of internal deterioration in the trailing edge after 190 hours.

The plates and vanes utilized for these evaluations were fabricated from Cb-1Zr alloy due to the shortage of program T222 for tests. The NS-1 coating had been previously observed to provide longer oxidation life over T222 than over Cb-1Zr.

The results of the test are adequate to indicate the effectiveness of the coatings. The major coating inconsistency is in the non-uniformity of the upper and drain edges. This variation in coating thickness can be corrected by developing double dipping techniques with specimen reversal or by building up the upper edge by spray coating after dipping.



Vane 1

Magnification: ~6X

Vane 1

Magnification: ~6X

FIGURE 93. FLAW IN BOND OF SPRAY COAT TO DIP COAT AFTER SILICIDING

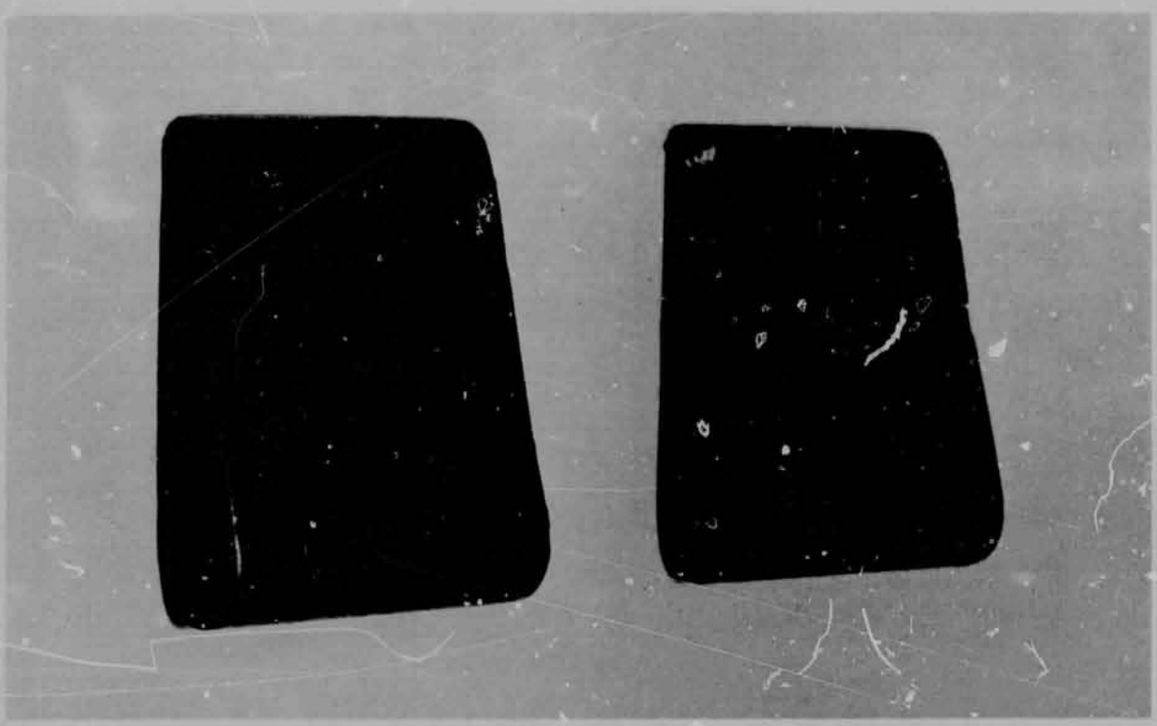
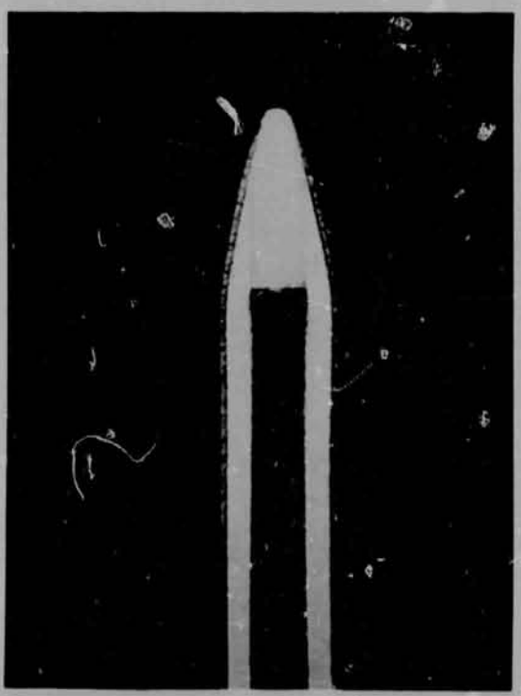


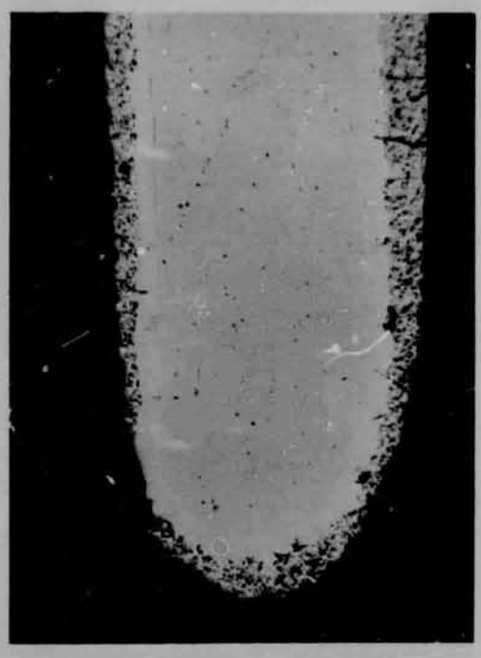
FIGURE 94. DIP COATED VANES AFTER 190 HOURS OF 1600°F CYCLIC OXIDATION



Magnification: 5-1/2X

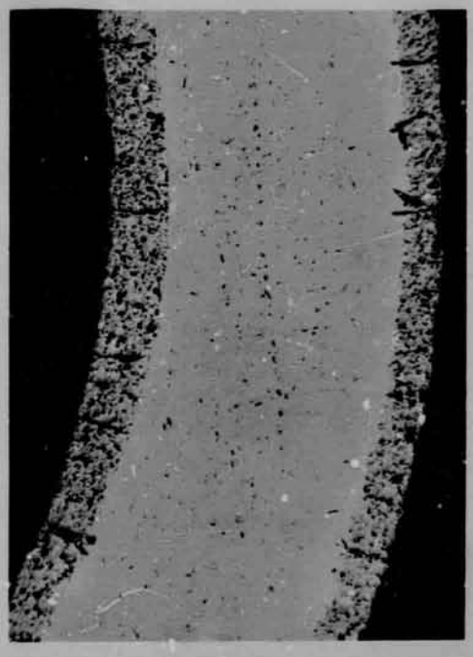
FIGURE 95. TRAILING EDGE OF SIMULATED VANE AFTER 190 HOURS CYCLIC OXIDATION AT 1600°F

Corner Trailing Edge



Upper Withdrawal Edge

Magnification: 50X



Leading Edge

Drain Edge

Magnification: 50X

FIGURE 96. SIMULATED VANE AFTER 190 HOURS CYCLIC 1600°F OXIDATION. Cb-1Zr Substrate NS-1 Dip Coated.

4

CONCLUSIONS

The duplex, (W-Mo-V-Ti)-Si, coatings afford the longest furnace, cyclic oxidation lives (>800 hours at 2400° F and 1600° F) on T222 and FS-85 alloys of any coating system ever investigated; also the coatings appear to afford the longest protection in oxidation-erosion rigs at 2400° F (>230 one-hour cycles). The coatings are not, however, immune to early shank damage characteristic of silicide coatings exposed in oxidation-erosion rigs.

Long-term exposure (800 hours) on coated T222 or FS-85 alloys has relatively minor effect on the mechanical properties of the alloys. The losses in properties observed could be directly traced to the penetration of silicon into the substrate alloy and loss in alloy cross-section. Sintering of the modifier for 15 hours up to 3100° F had no effect on the mechanical properties of the T222 alloy; however sintering under these conditions embrittled the FS-85 columbium-base alloy. A temperature of 2940° F was the maximum sintering temperature for the FS-85 alloy.

A number of specific conclusions relative to the composition and properties of the coatings are noted below:

- The tungsten/molybdenum weight ratio can be varied widely (0.15 to 2.3 were evaluated) while still producing oxidation resistant coatings.
- The tungsten + molybdenum concentration was observed to perform well in the pre-sintered range of 70 to 90 weight percent and post-sintered range of 80 to 90 weight percent.
- Vanadium was observed to be essential in modifier alloys after sintering to prevent pest-type, low-temperature (1600° F) oxidation failure.
- Titanium was observed to contribute to modifier sintering, coating-substrate bonding, short-term oxidation resistance, and activation of alloys for siliciding (increased titanium content increased siliciding rate).
- Iron and nickel were observed to be effective sintering aids in the tungsten-molybdenum-vanadium-titanium system. These sintering aids can be removed from the coating by vaporization during vacuum sintering.

- With a 15-hour, 2760° F vacuum sinter, all detectable iron was removed from the modifier alloy.

- With a 15-hour, 2760° F or higher vacuum sinter, most of the titanium was removed from the modifier alloy.

- For modifiers sintered at 2760° F, the coating surface-connected pore volume in the as-silicided condition must be less than 12 percent to be oxidation resistant, particularly at 1600° F.

- High concentrations (such as 30 weight percent total) of both vanadium and titanium in the modifier slurry contribute to coating strength and resistance to impact.

- Resistance to impact damage increases with the addition of a sintering aid such as iron and titanium to the modifier alloy.

- Good oxidation resistance was obtainable with considerable variation in the coating thickness and microstructure. Diffusion of silicon completely through the modifier layer and into the substrate during siliciding did not appear to diminish oxidation resistance; on the contrary, it appeared to be desirable to react all modifier alloy with silicon.

- Modifier alloy total oxygen content should be maintained at 0.2 percent or less to insure reliable oxidation resistance of the silicide.

- The average powder particle size for elemental powder slip for spray application is best in the 2 micron range.

- The average powder particle size for elemental powder slip for dip coating looks promising in the 2 to 3 micron range.

- The pre-alloyed powder particle size in spray applied modifiers can be as large as 12 microns and still develop into oxidation resistant coatings when silicided.

- Hollow vanes can be satisfactorily dip coated so long as the faying edge has an internal radius equal to or greater than 0.030 inch.

- The modifier coating can be applied by dipping, but additional work is required to optimize the process for internal and external surface application.

A single best composition could not be selected from the experimental effort, but the composition NS-4 (50W20Mo15Ti15V)-Si performed very well on both the T222 and FS-85 alloys in furnace oxidation, oxidation-erosion, oxidation after impact, retained mechanical properties, and room temperature bend ductility after oxidation exposure at 1600° F and 2400° F and, therefore, represents one of the best of the 26 coatings evaluated. The recommended processing steps for this coating are:

- Spraying slip 2.5/1 E-4 vehicle to solids volume ratio
- Fineness ~2 micron average Fisher subsieve particle size
- Application by spraying
- Modifier weight-thickness: 60 to 80 mg/cm^2, 0.004 to 0.005 inch
- Sintering cycle: 2760° F to 2940° F for 15 hours in a cold wall vacuum furnace at a pressure of 10^{-5} to 10^{-6} Torr
- Siliciding cycle: 2150° F for 15 hours or to provide a silicon to modifier atomic ratio of >2.1
- Surface connected pore volume must be less than 12 volume percent

5

RECOMMENDATIONS

The following are important areas of investigation for the enhancement of overall performance of this family of (W-Mo-Ti-V)-Si coatings for tantalum- and columbium-base alloys:

- Sintering aids might profitably be explored in greater depth in order to lower the modifier sintering temperature and decrease vaporization losses of elements such as V and Ti. These sintering aids must increase interparticle bonding as well as bonding to the substrate. Iron and nickel as fugitive sintering aids appear particularly promising, but Ni-Si and Fe-Si eutectic addition should also prove effective.

- Sintering conditions might be further optimized in order to develop processing techniques less sensitive to the part size or configuration.

- The sintering times and temperatures could be further optimized by more detailed analysis of the vaporization of Ti, V and Fe or Ni to determine how they influence the final composition, coating porosity, bonding to the substrate, oxidation and impact resistance.

- Improved methods of part or specimen support is desirable to minimize modifier damage by sticking or variable composition by restricting vaporization of V, Ti, Fe, etc.

- Further development is required to effect protection of shanks of refractory metal blade alloys. The combination of an oxygen diffusion barrier plus a ductile overlay for the root area appears to be a potential method to resist low-temperature oxidation (to 2000° F) and mechanical damage.

- For evaluation of coatings for vanes in oxidation-erosion rigs, a new technique for holding specimens to minimize mechanical damage is desirable.

- Application techniques require significant additional development. The most promising technique currently available for uniformly coating hollow shapes with a multi-element material is dip coating. Emphasis could be to:

- provide slips with controlled set
- optimize modifier element particle size
- improve coating uniformity by multiple dipping
- improve holding techniques

- Coating thickness should be optimized to relate thickness to performance.

- Quality control techniques (QCT) are required for each step in the coating application process together with a correlation of QCT with performance. QCT are most important for determining coating thickness and uniformity with particular emphasis on specimen corners and edges.

- Development of comminution for pre-alloyed modifier to produce powders in the 3 to 5 micron size is desirable. This would allow a better comparison between unalloyed and pre-alloyed modifiers. A pre-alloyed powder should be more applicable than unalloyed powders due to uniform particle density and properties of the particles.

- Additional mechanical property measurements are being made under NASA contract with Westinghouse with particular emphasis on strain rate sensitivity and stress rupture. Low-cycle fatigue and thermal fatigue data are lacking for these systems.

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2. Air Force Materials Symposium, 9-11 June 1965. Technical Papers AFML-TR-65-29, pp. 307-326.

3. A. R. Stetson and A. G. Metcalfe, "Development of Coatings for Columbium Base Alloys, Part I - Basic Property Measurements and Coatings System Development", AFML-TR-67-139 (Sept. 1967).

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5. W. D. Wood, H. W. Deem, and C. F. Lucks, "The Emittance of Ceramics and Graphites", DMIC Memorandum 148, March 28, 1962.

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APPENDIX A

SPECIFICATION FOR THE FS-85 ALLOY

1.0 SCOPE

1.1 Scope. This specification covers FS-85 (Cb-27Ta-10W-1.0Zr) alloy in bar form intended for high temperature structural applications.

2.0 APPLICABLE DOCUMENTS

2.1 Government Documents. None

2.2 Non-Government Documents.

ASTM Designation E29-58T (1958)	Recommended Practices for Designating Significant Places in Specified Limiting Values

3.0 REQUIREMENTS

3.1 Acknowledgments. The vendor shall mention this specification in all quotations and all purchase order acknowledgments.

3.2 Manufacture. Material covered by this specification shall be made from ingots which have been double vacuum melted by the electron beam and/or consumable electrode arc melting processes. Breakdown operations shall be performed with conventional extrusion, forging and rolling equipment normally found in primary ferrous and nonferrous plants.

3.3 Processing. The starting stock size, processing temperatures, percentages of reduction, in-process annealing temperatures and times shall be selected by the vendor. The amount of total reduction from the turned ingot to the final product shall exceed 75%. The amount of final reduction for each mill product, imparted just prior to the final vacuum heat treatment and the total reduction since the previous recrystallization anneal, shall be reported in the certificate of compliance.

3.4 Condition.

3.4.1 General. The finished product shall be supplied in the recrystallized condition throughout the cross-sectional area.

3.4.2 Heat Treatment. All annealing shall be carried out in a vacuum of less than 1×10^{-5} Torr. The conditions of final annealing shall be reported in the certificate of compliance.

3.4.3 Contamination. All items are to be free of contamination or internal oxidation. After final heat treatment, the material shall be examined metallographically for evidence of possible contamination caused by unsatisfactory heat treating atmospheres or processing conditions. A microhardness traverse shall show a hardness increase not greater than 50 VHN from the center to the surface of a cross-sectional sample of the final product. At the discretion of the purchaser, samples taken to include at least one surface of the final product, and not exceeding 0.050-inch thick, may be chemically analyzed by the purchaser for oxygen, nitrogen, hydrogen and carbon. The analyses shall not exceed the limits set forth in paragraph 3.5.3. Any indication of contamination shall be cause for rejection of all material represented by that sample. The material shall be acceptable if the contaminated layer is completely eliminated before shipment by a machining operation within the specified dimensions and tolerances.

3.5 Chemical Composition.

3.5.1 Ingot/Billet Composition. The chemical composition of ingots and billets for conversion to finished products shall conform to Table I (page 3). A minimum of four analyses shall be obtained as follows: ingot top-center, mid-radius and edge, and ingot bottom-center; all analyses must conform to ranges stated in Table I.

3.5.2 Final Product Composition. The manufacturer's ingot analyses shall be considered the chemical analysis for products supplied under this specification (Table I) except carbon, oxygen, nitrogen and hydrogen content which shall be determined in the finished product.

TABLE I

CHEMICAL COMPOSITION
FS-85 (Cb-27Ta-10W-1.0Zr) ALLOY

Element	Minimum Content ppm	Maximum Content ppm
Carbon	--	100
Nitrogen	--	100
Oxygen	--	--
Hydrogen	--	10
Molybdenum	--	200
Nickel	--	50
Cobalt	--	50
Iron	--	50
Vanadium	--	20
Tungsten	9%	11%
Tantalum	25%	28%
Zirconium	0.75	1.25
Columbium	Balance	--

3.5.3 Check Analysis. Finished product analysis shall not exceed the following limits or variations:

Element	Check Analysis Limits, Max., ppm	Permissible Variations in Check Analysis, ppm
Carbon	100	±10
Oxygen	150	±20
Nitrogen	100	±10
Hydrogen	15	± 2

3.6 Tolerances.

3.6.1 Rod.

3.6.1.1 Dimensions. Rod dimensions shall conform to the following tolerances:

Diameter	Length
± 0.010-inch or ± 5% whichever is less	± 0.125-inch

3.7 Reports. The manufacturer shall supply at least three copies of a report showing non-proprietary manufacturing methods, processing conditions, and test procedures and results for each lot of material in the shipment. The report shall also include the number of the specification and the purchase order or contract number.

4.0 MAXIMUM ALLOWABLE DISCONTINUITIES

4.1 General. The finished product shall be visibly free from oxide or scale of any nature, grease, oil, residual lubricants, and other extraneous materials. Cracks, laps, seams, gouges, and fins shall be unacceptable.

4.2 Porosity and Inclusions. Indications of internal porosity and non-metallic inclusions greater than 0.020-inch or 3% of the thickness, whichever is smaller, shall be unacceptable. Those indications in the range 0.010-inch to 0.020-inch or 2% of the thickness, whichever is smaller, shall be a minimum of 0.500-inch apart; those indications less than 0.010-inch shall be a minimum of 0.12-inch apart.

4.3 Surface Rework. All surface pores, gouges and other defects deeper than 0.005-inch or 3% of the thickness, whichever is smaller, shall be unacceptable. Surface imperfections may be faired smooth to remove any notch effect provided dimensional tolerances are still maintained.

5.0 QUALITY ASSURANCE PROVISIONS

5.1 Vendor Responsibility. The manufacturer shall make all tests and inspections of the material covered by this specification before shipment, unless otherwise specified. All test and inspection results shall be furnished to the purchaser.

5.2 Sample Selection. Care shall be exercised to insure that the samples selected for chemical analyses are representative of the material and uncontaminated by the sampling procedure. If there is any question about the sampling technique or the analysis, the methods for sampling and analysis shall be those agreed to by the buyer and seller. The location of test samples shall be reported in the certificate of compliance.

5.3 Test Methods.

5.3.1 Chemical Analysis. Chemical analyses shall be conducted by mutually acceptable procedures, such as the vacuum fusion methods for gases, the combustion method for carbon, and the spectrochemical methods for metallic elements.

5.4 Retest and Rework.

5.4.1 Surface Contamination. Any sample or specimen exhibiting obvious surface contamination or improper preparation which disqualifies it as a truly representative sample shall be replaced with a new sample.

5.4.2 Rework. If inspection and test results of a lot do not conform to the requirements of this specification, the lot may be re-worked at the option of the manufacturer. The lot shall be acceptable if all test results, after reworking, conform to this specification.

6.0 PREPARATION FOR DELIVERY

6.1 Identification. Each bundle, box, or carton shall be legibly and conspicuously marked or tagged with the number of this specification, purchase order or contract number, type, ingot number, lot number, nominal size, and the gross, net, and tare weights. When each bundle, box or carton consists of components from more than one ingot number or lot number, each component shall be identified individually.

6.2 Packing. Each individual item shall be wrapped in heavy gauge polyethylene film or other similar material and packed in a manner assuring safe delivery when properly transported by any common carrier.

7.0 DEFINITIONS

7.1 Lot. A lot shall include all material of the same size, shape, condition and finish from one heat of material and which has received the same

processing, has been annealed in the same vacuum annealing charge and has been processed simultaneously in all operations in which temperatures may reach 500°F or above. When process temperatures and environments are closely controlled or when closely adjacent sizes receive similar processing, lots may be combined for chemical, tensile and stress-rupture tests only, provided prior written approval has been obtained from the Solar Division of International Harvester Company.

7.2 Check Analysis. An analysis may be requested by the purchaser of the metal after it has been processed into finished mill forms, to verify the composition within a heat or lot. Check analysis tolerances do not broaden the specified heat analysis requirements but rather cover variations between laboratories in the measurements of the chemical content.

7.3 Significance of Numerical Limits. For determining compliance with the specified limits for requirements of the properties listed below, and observed value or a calculated value shall be rounded off using the rounding-off method in ASTM Designation E29-58T, "Recommended Practices for Designating Significant Places in Specified Limiting Values".

Test	Rounded-Off Unit for Observed or Calculated Value
Chemical composition and dimensional tolerances (when expressed decimally)	Nearest unit in the last right-hand place of figures of the specified limit

APPENDIX B

PROCEDURES FOR HYDRIDING TITANIUM AND VANADIUM

Hydriding Titanium

The titanium sponge (-20 + 50 mesh) is placed in an unlined Inconel retort which is subsequently sealed by fusion welding. Following pressurizing of the retort to 5 psig with argon, the welds are soap-bubble leak checked. The retort and the palladium alloy hydrogen purifier are vacuum-argon cycle purged a minimum of three times. Under dynamic vacuum, the hydrogen purifier is heated to 850°F at which point it is back filled with hydrogen. The retort is then vacuum-hydrogen cycle purged a minimum of three times at room temperature before the hydrogen pressure in the retort is adjusted to 10 mm Hg above atmospheric pressure preparatory to placing the retort in a furnace preheated to 800°F. The furnace containing the retort is then heated to 1250°F over a 30-minute period. The retort is soaked in the furnace at 1250°F for one hour. The hydriding reaction, however, should be complete in 30 to 40 minutes at 1250°F, as indicated by the flow meter in the hydrogen supply line from the palladium purifier. The hydrogen pressure is maintained above atmospheric pressure while the retort is removed from the furnace and allowed to cool to room temperature.

Hydriding Vanadium

Vanadium granules (-1 + .5 inch sponge) are pickled in nitric acid rinsed in distilled water and subsequently methanol. After vacuum drying at room temperature the vanadium is placed in an Inconel retort which is sealed by fusion welding. After pressurization with argon, the retort is soap-bubble leak checked. The retort and palladium hydrogen purifier are vacuum-argon cycle purged a minimum of three times. After evacuation, the palladium membrane is heated and the retort vacuum-hydrogen purged as recommended in the "Hydriding Titanium" section.

With the hydrogen pressure from the palladium alloy purifier adjusted to 10 mm Hg above atmospheric pressure, the retort is inserted into a furnace preheated to 1200°F. The furnace is then heated to 1700°F over a one-hour period and held at temperature for a period of not less than 12 hours. After the 1700°F soak, the control temperature is reduced to 1100°F. Eight hours later the furnace control is reduced to 500°F. When it reaches 500°F it is removed from the furnace and allowed to air cool while maintaining a hydrogen pressure above atmospheric pressure.

APPENDIX C

SPRAY SLURRY PREPARATION PROCEDURE

A description of the process used in preparing the slurries based on a vehicle containing an ethyl cellulose binder is given in the following paragraphs.

Thirty grams of ethyl cellulose[1] is dissolved in a mixture of 200 cc of secondary butyl alcohol and 800 cc of xylene. One thousand cc of Stoddard solvent (a petroleum distillate having a boiling point range of 312 to 390°F is added to this solution to obtain the desired vehicle, which was designated E4.

Between 180 and 220 cc of the vehicle and the appropriate quantity of powdered elemental metals needed to give a fluids-to-solids true volume ratio of 2.5 are added to a one-quart low-silica ball mill[2] that is slightly more than half filled with balls.

After the ball mill has been tumbled for a period of 20 hours, the slip is transferred to a preweighed graduated cylinder to allow for the determination of the specific gravity (by weighing the observed volume of slip) prior to spray application.

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1. N-200 grade ethyl cellulose was supplied by the Polymers Department, Hercules Powder Company, Wilmington, Delaware.

2. Burundum-fortified ball mills and balls were supplied by the U. S. Stoneware Company, Akron, Ohio.

APPENDIX D

DIP SLURRY PREPARATION PROCEDURE

A description of the process used in preparing the dip slurries, based on a vehicle composed of xylene and ethyl cellulose binder, is given in the following paragraphs.

Twenty grams of N-22 and 30 grams of N-7 ethyl cellulose[1] are dissolved in 1000 cc of xylene to obtain the desired vehicle, which was designated NSV-1.

Approximately 1000 grams of the powdered elemental metals in the NS-1 modifier (or an equivalent volume of another composition) and 500 cc of the vehicle E-4 (Ref. App. C) are added to a three-quart high alumina, low-silica ball mill[2] that is approximately half-filled with balls. After the ball mill has been tumbled for a period of 20 to 40 hours, a sample of the powder is obtained by vacuum filtration of a portion of the slurry. The metal powder, after 20 hours of vacuum drying is evaluated by utilizing the Fisher Subsieve Analyzer to determine particle size.

When the powder has been milled to the desired average particle size (< 3 microns as determined by the Fisher Subsieve analysis), the slurry is vacuum filtered, washed with xylene and acetone, and the powder product vacuum dried for 40 hours.

Between 180 and 220 cc of the NSV-1 vehicle is placed in a 500 cc glass jar and the appropriate quantity of powdered elemental metals needed to give a fluid-to-solids true volume ratio of 2 is blended into the vehicle. After the glass jar has been argon purged and sealed, it is tumbled for a period of 20 hours. The slip is transferred to a pre-weighed graduated cylinder to allow for the determination of the specific gravity (by weighing the observed volume of slip). With the specific gravity, it is possible to determine the true vehicle to solids ratio for the slip. Additional vehicle is then added as required to produce a slip with a vehicle-to-solid ratio of approximately 2.5/1 for an average particle size of three microns. The amount of vehicle required for the slip cannot be quantitatively pre-specified as it varies with powder particle size, powder density, temperature, etc. The final criteria that controls this addition is bisque retention on a test dip coated specimen. The slip is adjusted to give a retention of 0.06 to 0.07 grams/cm^2 for NS-1.

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1. N-22 and N-7 ethyl cellulose were obtained from the Polymers Department, Hercules Powder Company, Wilmington, Delaware.

2. Burundum-fortified ball mills and balls were supplied by the U. S. Stoneware Company, Akron, Ohio.